REMARKS

I. Status and Disposition of the Claims

A. Status of the Claims

Claims 1-93 are pending. Claims 41-45, 48-62, 66-78, 87-89, 92, and 93 are withdrawn from consideration pursuant to a Requirement for Restriction and Election of Species. See Office Action, pages 2 and 9. Applicant notes that at page 9 of the Office Action, the Examiner indicates that claims 46 and 47 are also withdrawn from consideration, despite Applicant's statement at page 4 of the May 23, 2007, Response to Restriction Requirement, that such claims are drawn to the elected group and species. Therefore, Applicant assumes this listing of the claims was in error and claims 46 and 47 are under consideration on the merits unless the Examiner provides a specific explanation as to why said claims should be withdrawn. To the extent the rejections set forth in the Office Action are applicable to these claims, Applicant's arguments set forth below are also deemed applicable. Thus, claims 1-40, 46, 47, 63-65, 79-86, 90, and 91 are pending and under consideration on the merits.

Applicant has amended claims 32-36 to correct a typographical error, thereby maintaining strict antecedent basis, and to clarify the claim language. In particular, these claims have been amended to insert a negative (-) sign before the first endpoint of the claimed ranges, and to replace the term "Tg" with " glass transition temperature." Support for these amendments may be found in the as-filed specification, for example, at page 15, paragraph [063]. Accordingly, these amendments raise no issue of new matter.

B. Summary of the Office Action

In the Office Action, the Examiner:

• Indicates that a certified English language translation of the priority document, Provisional U.S. Application No. 60/459,259, must be submitted to perfect Applicant's claim of priority (*See* Office Action, page 10);

• Rejects claims 32-39 under 35 U.S.C. § 112, second paragraph, as allegedly indefinite (*See id.* at 10-11);

• Rejects claims 1-40, 63-65, and 79-86 under 35 U.S.C. § 102(b) as allegedly anticipated by U.S. Patent No. 5,527,840 ("Chutko") (*See id.* at 11-12); and

• Rejects claims 90 and 91 under 35 U.S.C. § 103(a) as allegedly unpatentable over U.S. Patent No. 6,113,881 ("Bhatt") in view of Chutko (*See id.* at 13-14).

In response, Applicant submits the following remarks.

II. Priority Claim

As noted above, the Examiner indicates that a certified English language translation of U.S. Provisional Application No. 60/459,259 is necessary to perfect Applicant's claim of priority under 35 U.S.C. § 119(e). Office Action, page 10. The Examiner further contends that "a specific reference to the prior-filed application in compliance with 37 CFR 1.78(a) must be included in the first sentence(s) of the specification following the title or in an application data sheet." *Id.* In the present case, Applicant timely claimed, upon filing of this application, benefit under 35 U.S.C. § 119 of U.S. Provisional Application No. 60/459,259, filed April 2, 2003, including reference to the provisional application in the first sentence of the present application. *See* [001] of as-filed specification. To perfect this claim of priority, Applicant now files concurrently herewith a certified English language translation of U.S. Provisional Application No. 60/459,259 in that application. A copy of the "Submission of English Language

Translation of Provisional Application Under 37 C.F.R. § 1.52(d)(2)" coversheet is provided to the Examiner with the present filing. *See* Exhibit 1. In view of this submission, Applicant believes that her claim of priority is perfected.

III. Rejections

A. 35 U.S.C. § 112, Second Paragraph, Rejection of Claims 32-39

The Examiner rejects claims 32-39 under 35 U.S.C. § 112, second paragraph, alleging that these claims are ambiguous, and requesting a "detailed explanation" as to which monomers possess the claimed glass transition temperature. *See id.* at 11. Further, the Examiner alleges that the glass transition temperatures recited in claims 33-35 lack antecedent basis.

Regarding the alleged lack of antecedent basis, Applicant respectfully submits that the Examiner's position is overcome by the above amendment to claims 32-36. Accordingly, Applicant respectfully requests withdrawal of at least this portion of the § 112, second paragraph, rejection.

As to the Examiner's allegation that claims 32-39 are ambiguous, Applicant respectfully disagrees. Contrary to the Examiner's implication, it is not necessary to define specific monomers having the claimed glass transition temperature in order to comply with 35 U.S.C. §112, second paragraph. Rather, an applicant need only utilize claim terminology that is sufficiently clear as to apprise "one of ordinary skill in the art of its scope and, therefore, [serve] the notice function required by 35 U.S.C. 112, second paragraph, by providing clear warning to others as to what constitutes infringement of the patent." MPEP §2173.02.

Here, one of ordinary skill in art would have no difficulty interpreting the metes and bounds of the terminology of claims 32-39. Indeed, one of ordinary skill in the art would understand the phrase "at least one monomeric residue resulting from at least one monomer which is capable of forming a homopolymer with a glass transition temperature less than or equal to 20°C" to mean precisely what it says. The mere fact that claims 32-39 do not recite the exemplary monomers set forth in the specification **does not** make them indefinite under 35 U.S.C. § 112, second paragraph, absent some showing or explanation as to why the claim language, absent such disclosure, is so unclear that one of ordinary skill could not discern the scope of the claims. Moreover, although Applicant does not believe further clarification is necessary, Applicant respectfully directs the Examiner to page 16, paragraphs [066]-[067], and pages 21-22, paragraphs [081]-[082], of the as-filed specification, which provide a myriad of non-limiting examples of monomers that may have the claimed glass transition temperature.

For at least the foregoing reasons, Applicant respectfully requests withdrawal of the §112, second paragraph, rejection.

B.   35 U.S.C. § 102(b) Rejection of Claims 1-40, 63-65, and 79-86

According to the Examiner, Chutko expressly teaches each and every element of claims 1-40, 63-65, and 79-86, with the exception of the claimed properties, e.g., polydispersity index, elastic recovery, and/or Young's modulus. *See* Office Action, pages 11-12. Nonetheless, the Examiner maintains that all of these claims are anticipated by Chutko, because the "[p]atent office is not equipped to measure" these properties and evidence has not been presented to the contrary. *See id.* at 12.

Applicant respectfully disagrees and traverses this rejection for at least the following

reasons.

It has long been held that to establish anticipation under 35 U.S.C. §102(b), an

examiner must establish that a reference teaches, either expressly or inherently, each

and every element of a claim. *See* M.P.E.P. § 2131 (citing *Verdegaal Bros. v. Union Oil*

Co. of California, 814 F.2d 628, 631 (Fed. Cir. 1987)). Further, a rejection under § 102

is proper **only** when the claimed subject matter is **identically** described or disclosed in

the prior art. *See In re Arkley*, 455 F.2d 586, 587 (CCPA 1972) (emphasis added). As

discussed below, the Examiner has failed to meet this burden in the present case.

Independent claim 1 recites, *inter alia*, "[a] hair-cosmetic composition comprising,

in a cosmetically acceptable medium, at least one film-forming **gradient**

copolymer. . . ." As described in the as-filed specification, "[g]radient copolymers are

copolymers wherein the ratio of various monomers varies along the length of the chain.

See specification, page 7, paragraph [031]. In particular, the specification explains that

"[t]he at least one film forming gradient polymer . . . includes at least two different

monomeric residues, whose concentration along the polymer chain **changes gradually,**

in a regular and predictable manner." *Id.* at page 7, paragraph [032]. Contrary to the

Examiner's assertions, Chutko does not teach or fairly suggest such a polymer.

Chutko is drawn to an aqueous coating composition that includes at least about

50% by weight of a solvent component, and at least 30% by weight of a film-forming

component. *See* Chutko, column 3, lines 22-25. Chutko discloses the use of a carboxy

addition polymer ("CAP") as the film-forming component. *See id.* at column 4, lines 21-

25. In one example, the CAP is formed by reacting 1160 parts ethyl acrylate, 1864

parts acrylic acid, 2480 parts styrene, and 432 parts 70% benzoyl peroxide. *See id.* at

column 7, lines 50-67. Although Chutko does not disclose the precise mechanism for

forming the CAP, it appears to be conventional radical polymerization, as 1) Chutko

indicates that the CAP is formed by "conventional polymerization processes[,]" and 2)

benzoyl peroxide is a well known initiator of radical polymerization. *See* Chutko, column

4, lines 35-45, column 7, lines 50-67; "Radical Polymerization," Concise Encyclopedia of

Polymer Science and Engineering, J. Kroscwitz, ed., page 947 (1990).[1] However,

Chutko is completely silent with respect to the type of polymer (i.e., random, block,

gradient, etc.) formed by the disclosed polymerization process. Indeed, Chutko makes

no mention of the structure of the disclosed CAP whatsoever.

Applicant acknowledges that the Examiner may be relying on the doctrine of

inherency in support of the anticipation rejection. However, Applicant respectfully

submits that the Examiner has not even alleged, much less established a viable theory

that Chutko's disclosed CAP polymer is a gradient copolymer. In particular, the

Examiner has not explained why Chutko's "conventional" radical polymerization process

will **necessarily** result in a gradient copolymer, as opposed to some other polymeric

form, e.g., a block or random copolymer. *See* M.P.E.P. § 2131.01(III). Rather, as

Applicant explains in the specification, "conventional" radical polymerization processes,

like those disclosed in Chutko, tend to result in random or block copolymers, which are

not the same as the claimed gradient copolymers. *See* specification, pages 6-9,

paragraphs [028]-[035].

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[1] A copy of this reference is attached herewith as Exhibit 2 for the Examiner's
convenience.

Finally, Applicant respectfully points out that Chutko is drawn to compositions and methods that are suitable for coating **metal substrates**. *See* Chutko, abstract. Thus, Chutko does not teach or even suggest a hair-cosmetic composition, as claimed. *See* Claim 1. Moreover, Chutko does not provide any indication that the disclosed composition may be reformulated so as to be suitable for use as a hair-cosmetic composition in a cosmetically acceptable medium.

For at least the foregoing reasons, Chutko does not teach, expressly or inherently, each and every element of claims 1-40, 63-65, and 79-86. Accordingly, the rejection of these claims is improper, and Applicant respectfully requests that it be withdrawn.

C. § 103(a) Rejection of Claims 90-91

The Examiner alleges that claims 90-91 are "unpatentable over" Bhatt in view of Chutko for the reasons set forth at page 13 of the Office Action. In particular, the Examiner alleges that "it would be obvious to one of ordinary skill in the art at the time the invention was made to prepare compositions of [Bhatt] and use in the form of gel or sprays and substitute the film formers of [Bhatt] with film formers of [Chutko,] which teaches these polymers are used for coating." *See* Office Action, page 13.

In making a rejection under 35 U.S.C. § 103, the Examiner "bears the initial burden of factually supporting any *prima facie* conclusion of obviousness. *See* M.P.E.P. § 2142. In its decision in *KSR Int'l Co. v. Teleflex Inc.*, 127 S. Ct. 1727, 82 U.S.P.Q. 2d 1385 (2007), the Supreme Court confirmed that the "framework for applying the statutory language of §103" was still based on its landmark decision in *Graham v. John Deere Co. of Kansas City*, 383 U.S. 1, 148 U.S.P.Q. 459 (1966).

Under *Graham*, there are four factors for consideration when determining whether an invention is obvious:

(1) the scope and content of the prior art;

(2) the differences between the prior art and the claims at issue;

(3) the level of ordinary skill in the art; and

(4) secondary considerations.

383 U.S. at 17, 148 U.S.P.Q. at 467. However, the Court indicated that there is no necessary inconsistency between the idea underlying the teaching, suggestion, or motivation ("TSM") test and the *Graham* analysis. *KSR*, 127 S. Ct. at 1741, 82 U.S.P.Q. 2d at 1389. As long as the TSM test is not applied as a "rigid and mandatory" formula, the test can provide "helpful insight" to an obviousness inquiry. *Id.*

Applicant respectfully traverses this rejection, at least because even if, *arguendo*, Bhatt and Chutko can be properly combined in the manner asserted by the Examiner, which Applicant does not concede, the resultant combination does not possess each and every element of the present claims. As explained above, Chutko discloses a carboxy addition polymer formed from ethyl acrylate, styrene, and acrylic or methacrylic acid monomers. *See* Chutko, column 8, lines 3-10. However, Chutko does not disclose, expressly or inherently, that the resultant polymer is a gradient copolymer, as claimed. More specifically, Chutko forms the disclosed CAP by conventional radical polymerization. *See id.* at column 4, lines 35-40 and column 7, liners 50-67. Applicant explains in the specification that such polymerization tends to result in random or block copolymers, which are not the same as the claimed gradient copolymer. *See*

specification, pages 6-9, paragraphs [028]-[035]. Bhatt does not remedy this deficiency, nor does the Examiner allege that it teaches the claimed gradient copolymers.

Moreover, as noted above, Chutko is drawn to compositions that are suitable for coating metal substrates. *See* Chutko, abstract. In contrast, Bhatt is drawn to a hairstyling mousse composition. *See* Bhatt, column 1, lines 5-15. Given the vast difference in the stated applications, Applicant respectfully submits that one of ordinary skill in the art would not look to the hairstyling mousse art for solutions to problems that may occur in the metal coating art. Moreover, the Examiner has not provided any explanation as to **why** one of ordinary skill in the art would combine references from such divergent areas of technology, much less **why** they would enjoy a reasonable expectation of success in making such a combination.

For at least the foregoing reasons, Applicant respectfully submits that one of ordinary skill in the art would not look to Bhatt, which is drawn to hairstyling mousses, to correct problems or deficiencies of the technology disclosed by Chutko, i.e., metal coating compositions. Further, even if, *arguendo*, the combination of Bhatt and Chutko is proper, the resultant combination does not result in the claimed invention for the reasons discussed above. Accordingly, the rejection is improper, and should be withdrawn.

IV.   Conclusion

In view of the foregoing amendments and remarks, Applicant respectfully

requests reconsideration and reexamination of this application and the timely allowance

of the pending claims.

Please grant any extensions of time required to enter this response and charge

any additional required fees to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: April 14, 2008   By: *Courtney B. Meeker*
Courtney B. Meeker
Reg. No. 56,821

Attachments:

Exhibit 1:   Copy of Cover Page of April 14, 2008, Submission in U.S. Provisional
Application No. 60/459,259 (1 page)

Exhibit 2:   "Radical Polymerization," Concise Encyclopedia of Polymer Science and
Engineering, J. Kroscwitz, ed., pages 940-956 (1990).

The present invention relates to new hair-cosmetic
compositions containing special copolymers, especially
amphiphilic gradient copolymers, that are preferably
soluble or dispersible in water and/or in organic

5 solvents.

Styling compositions packaged in the form of an
aerosol spray generally contain a high proportion of
alcohol. Now, cosmetics with a high alcohol content are

10 under particular scrutiny, especially in the United
States, following the recent sensitization of public
opinion to the environmental problems resulting from
the emission of volatile organic products into the
atmosphere.

15 One solution for reducing the amount of alcohol,
or even eliminating alcohol from the formulations
completely, is replacement with an equivalent amount of
water. However, such addition of large amounts of water
to aerosol sprays intended for fixation of hair, such

20 as lacquers, leads to a considerable, undesirable
distortion of the hair and to a degradation of the
cosmetic properties. Moreover, most propellants of the
hydrocarbon type are incompatible with water and for
this reason it is generally impossible to use them in

25 compositions with a high water content.

Conventional radical polymers, i.e. those obtained
by classical radical polymerization, can be used for

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ENGINEERING

Methods for Studying Radiation-induced Oxidative Degradation. The methods described above for studying radiation degradation in an inert atmosphere also apply to degradation in the presence of air. Additional techniques are useful for monitoring oxidation, including ir spectroscopy and chemiluminescence. Special techniques have been developed for quantitatively profiling heterogeneous oxidation. Qualitative identification of heterogeneous oxidation can often be achieved by polishing the cross-sectional surface of a degraded sample; areas with different extents of oxidation are apparent on optical examination.

Dose-rate Effects. When polymeric materials are irradiated in the presence of oxygen, the rate of degradation and the nature of degradation can be strongly influenced by the dose rate. Lower dose rates often increase oxidation and chain-scission yields, and result in more extensive material degradation per equivalent absorbed dose. Dose-rate effects arise (*1*) due to oxygen diffusion effects, or (*2*) whenever one or more steps in the oxidation chemistry become rate-limiting on a time scale comparable to oxygen diffusion, peroxide breakdown, and radical migration.

Postirradiation Effects. Degradation of irradiated materials often continues, in storage or in use, long after the material has been removed from the radiation environment. This effect is caused by continuing free-radical-mediated oxidation. Significant postirradiation oxidation effects may take place over weeks or years, and may result in degradation that is much more extensive than that which was the immediate effect of the irradiation.

Temperature Effects. In the presence of oxygen, temperature often influences radiation degradation. Strong temperature effects can arise caused by changes in the rate of key processes that affect the oxidation, such as peroxide decomposition, radical migration, oxygen diffusion, diffusive loss of stabilizer additives, and others.

Stabilizers for Radiation-oxidative Degradation. The resistance of most polymers to radiation oxidation is significantly improved by stabilizers. The stabilization effect can be larger than that achieved by inert-atmosphere irradiation. Stabilizers are usually antioxidants, particularly radical scavengers, that interrupt the radical-mediated oxidation chain reaction.

Radiation Resistance of Specific Polymers. Many materials exhibit much less resistance to radiation under oxidizing conditions, and it would be convenient to have tables of radiation resistance in air available. However, this becomes extremely complicated because of parameters that play no role (or have a comparatively smaller effect) under inert atmosphere, but that dramatically affect the radiation resistance of polymers in air. These parameters include dose rate, material thickness and geometry, formulation (particularly stabilizers), temperature, and postirradiation time. For most polymers, data referring to these variables are scant. Figure 1 illustrates the complexity that emerges when radiation resistance is evaluated under different conditions.

Accelerated Radiation-degradation Tests. Because of the limited data available and the strong influence of many factors specific to material type, sample geometry, and environmental variables, prediction of the radiation resistance of a specific material in air under particular environmental conditions usually requires a laboratory aging test. Most time scales of practical importance span years and require accelerated aging techniques. Accelerated tests are run under short-term, high stress-
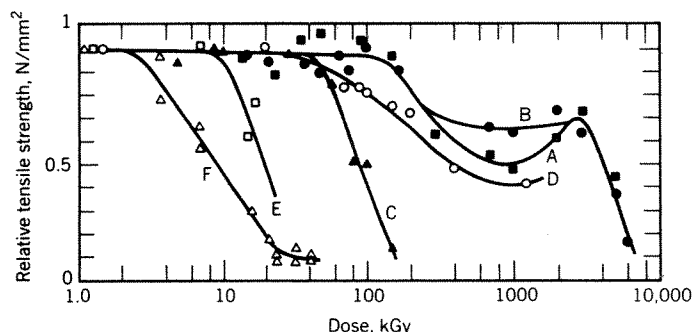

Figure 1. Changes in relative tensile strength of a polypropylene material as a function of irradiation. A, 0.3-mm sample thickness, irradiated at 5×10^6 Gy/h under vacuum; B, 0.3-mm sample thickness, irradiated at 5×10^6 Gy/h under vacuum, followed by heating 1 h at 80°C; C, 0.3-mm sample thickness, irradiated in air at 10^4 Gy/h; D, 1.0-mm sample thickness, irradiated in air at 10^6 Gy/h and left standing two months before testing; E, 1.0-mm sample thickness, irradiated in air at 4 Gy/h; F, 0.4-mm diameter wire, irradiated in air at 4 Gy/h (1 Gy = 100 rad). To convert N/mm² to psi, multiply by 145.

rate conditions that are higher than in the application environment. However, precisely those parameters that must be altered to achieve an accelerated test are also the parameters that can dramatically affect degradation rates and behaviors, and therefore the design and interpretation of accelerated aging experiments is complicated. A number of methodologies have been developed for this purpose.

BIBLIOGRAPHY

A. Charlesby, *Atomic Radiation and Polymers,* Pergamon Press, Elmsford, N.Y., 1960.

A. Chapiro, *Radiation Chemistry of Polymeric Systems,* Wiley-Interscience, New York, 1962.

M. Dole, ed., *The Radiation Chemistry of Macromolecules,* Academic Press, New York, Vol. 1, 1972, and Vol. 2, 1973.

F. A. Makhlis, *Radiation Physics and Chemistry of Polymers,* John Wiley & Sons, Inc., New York, 1975.

ROGER CLOUGH
Sandia National Labs

RADIATION-SENSITIVE POLYMERS. See RADIATION-RESISTANT POLYMERS.

RADICAL-ION. See ANIONIC POLYMERIZATION.

RADICAL POLYMERIZATION

Free radical polymerization has received more intensive study than any other chemical chain reaction; countless investigations have contributed to industry and to the chemistry of free radicals. Advances in both fields continue to be made, with a particular emphasis on the growth of special polymers. These require more refined synthetic routes and are often necessarily free-radical on account of the reactive natures of "active" com-

ponents. Nevertheless, free-radical polymerization still accounts for a large proportion of mass-produced polymers: in 1985 over 46% (by weight) of the total U.S. production of plastics involved this type of polymerization. Currently, optimizing established processes is a primary and continuing endeavor.
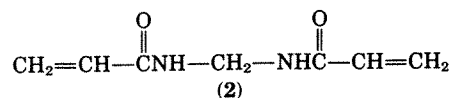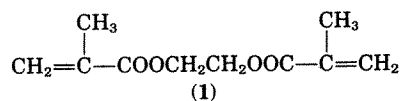
Monomers

Monomers in free-radical polymerization are commonly monosubstituted or unsymmetrically (1,1-) disubstituted ethylenes, CH_2=CHX or CH_2=CXY. The essential polymerization step is repeated free-radical addition to monomer double bonds, forming chains of carbon atoms constructed of units
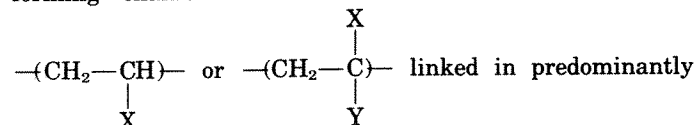
$$-(CH_2-\underset{\underset{X}{|}}{C}H)- \quad \text{or} \quad -(CH_2-\underset{\underset{Y}{|}}{\overset{\overset{X}{|}}{C}})- \quad \text{linked in predominantly}$$

head-to-tail fashion (the substituted carbon atom being designated the head).

The substituents X,Y in an olefinic monomer form sidechains attached to the primary chains of the polymer. There are few restrictions on the nature of the substituents. These groups determine the reactivities of the propagating radicals and monomers and also, to a large extent, the properties of the final polymers.

Dienes constitute an important class of vinyl monomers. Those having isolated double bonds are typified by p-divinylbenzene, ethylene glycol dimethacrylate (1), and N,N'-methylenebisacrylamide (2). Either one or both double bonds may participate in polymerization; when both react, cross-linked structures are generated which confer enhanced mechanical properties and increased solvent resistance on the products.

$$CH_2=\underset{\underset{CH_3}{|}}{C}-COOCH_2CH_2OOC-\underset{\underset{CH_3}{|}}{C}=CH_2$$
$$(1)$$

$$CH_2=CH-\overset{\overset{O}{\|}}{C}NH-CH_2-NH\overset{\overset{O}{\|}}{C}-CH=CH_2$$
$$(2)$$

Special structural features in the substituents may induce major participation in polymerization, for example the presence of highly strained rings or rings that on opening form very stable groups such as carbonyl.

Free-radical polymerizations are normally effected in the liquid phase, in bulk monomer, or in solution; for commercial large-scale preparations solution, suspension, or emulsion polymerizations have many advantages, eg, effective heat dissipation, and are frequently employed (see SUSPENSION POLYMERIZATION; EMULSION POLYMERIZATION).

As a result of its great versatility and relative simplicity, free-radical polymerization is employed in the synthesis of countless homo- and copolymers with properties distributed over an almost unlimited range.

Component Reactions

A typical free-radical polymerization comprises four elementary steps: initiation, propagation, termination, and chain transfer.

In initiation, a free radical $\dot{R}_0$ derived from an initiator, the

"primary radical," adds to a monomer molecule to form an active center, a free radical that subsequently propagates (eq. 1):

$$\dot{R}_0 + CH_2{=}CXY \longrightarrow R_0{-}CH_2{-}\dot{C}XY \qquad (1)$$
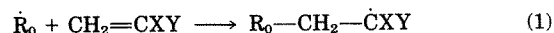
Other initiating reactions, such as addition to the head of the molecule

$$\dot{R}_0 + CH_2{=}CXY \longrightarrow R_0{-}CXY{-}\dot{C}H_2 \qquad (1a)$$
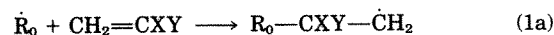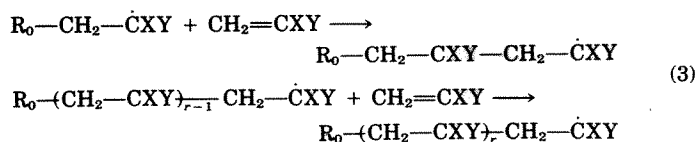
or hydrogen abstraction, are possible but less common; their importance depends on the structures of the radical and the monomer.

Propagating radicals are denoted here by $\dot{R}_r$, in which the subscript indicates the number of monomer units which have added to the initial radical $\dot{R}_0$. Thus if M represents a monomer molecule, equations 1 and 1a may be summarized as

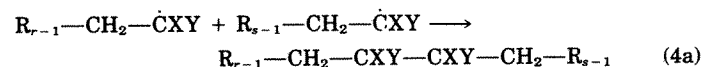$$\dot{R}_0 + M \longrightarrow \dot{R}_1 \qquad (2)$$
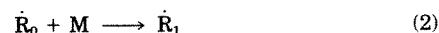
The propagation or growth reaction consists of the (rapid) addition of monomer molecules to the radical species. Usually it occurs in head-to-tail fashion, as indicated in equations 3:

$$R_0{-}CH_2{-}\dot{C}XY + CH_2{=}CXY \longrightarrow$$
$$R_0{-}CH_2{-}CXY{-}CH_2{-}\dot{C}XY$$
$$(3)$$
$$R_0{-}(CH_2{-}CXY)_{r-1}CH_2{-}\dot{C}XY + CH_2{=}CXY \longrightarrow$$
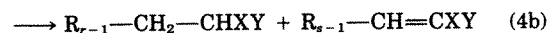$$R_0{-}(CH_2{-}CXY)_r{-}CH_2{-}\dot{C}XY$$

However, as with initiation, alternatives are possible and head-to-head, tail-to-head, and tail-to-tail modes occur, usually to minor extents (see HEAD-TO-HEAD POLYMERS).

In termination, growth of polymer chains is brought to an end by the destruction of propagating radicals. Normally, in the absence of retarding species that destroy growing radicals, chain termination occurs by bimolecular interaction of radicals. These processes, analogous to those taking place with simple alkyl radicals, consist of radical combination (eq. 4a) or disproportionation (eq. 4b):

$$R_{r-1}{-}CH_2{-}\dot{C}XY + R_{s-1}{-}CH_2{-}\dot{C}XY \longrightarrow$$
$$R_{r-1}{-}CH_2{-}CXY{-}CXY{-}CH_2{-}R_{s-1} \qquad (4a)$$
or
$$\longrightarrow R_{r-1}{-}CH_2{-}CHXY + R_{s-1}{-}CH{=}CXY \qquad (4b)$$

In these and many subsequent equations, the number of monomer units in R (or $\dot{R}$) is denoted by a subscript, eg, r. Disproportionation leads to two polymer molecules, one saturated and one containing a terminal double bond; the hydrogen atom transferred need not come from a methylene group as in equation 4b but may originate in an X or Y substituent. Many monomers show both types of termination; thus in methyl methacrylate, disproportionation is approximately twice as rapid as combination at room temperature and increases in importance as the temperature is raised. On the other hand, styrene and acrylonitrile radicals terminate preponderantly by combination.

Atom (often hydrogen) abstraction from saturated molecules is a well-known reaction of free radicals and, as would

be expected, is important in free-radical polymerization. It leads to the chain-transfer process, first recognized by Flory in 1937, which brings about the cessation of growth of a propagating radical and at the same time produces a new small radical which may propagate. In general, the effect of chain transfer on the overall polymerization is determined by the reactivity of the transfer radical formed.
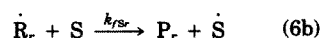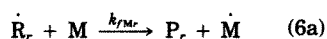
Chain transfer to polymer normally gives rise to branched or cross-linked molecules. Termination by combination or disproportionation yields cross-linked products or graft copolymers, respectively.
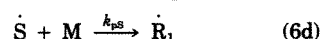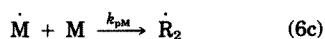

(5)
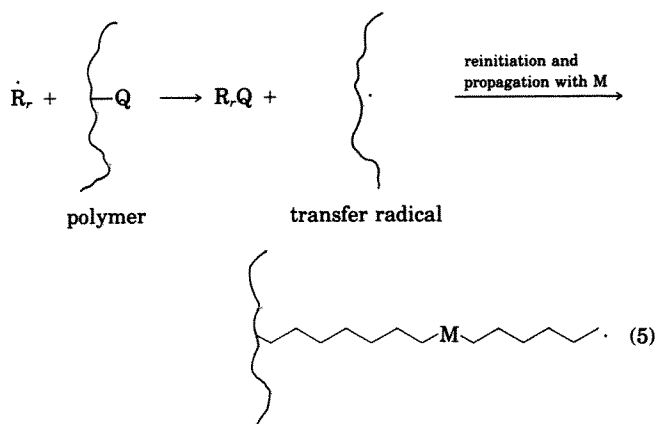
Ideal Polymerization Mechanism

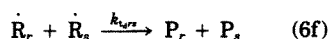The four component reactions discussed are set out formally in the following:

Transfer to monomer or substrate

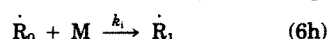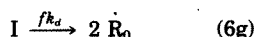$$\dot{R}_r + M \xrightarrow{k_{fMr}} P_r + \dot{M} \qquad (6a)$$

$$\dot{R}_r + S \xrightarrow{k_{fSr}} P_r + \dot{S} \qquad (6b)$$

Reinitiation by transfer radicals

$$\dot{M} + M \xrightarrow{k_{pM}} \dot{R}_2 \qquad (6c)$$

$$\dot{S} + M \xrightarrow{k_{pS}} \dot{R}_1 \qquad (6d)$$

Termination

$$\dot{R}_r + \dot{R}_s \xrightarrow{k_{t_c rs}} P_{r+s} \qquad (6e)$$

$$\dot{R}_r + \dot{R}_s \xrightarrow{k_{t_d rs}} P_r + P_s \qquad (6f)$$

Initiation

$$I \xrightarrow{fk_d} 2\,\dot{R}_0 \qquad (6g)$$

$$\dot{R}_0 + M \xrightarrow{k_i} \dot{R}_1 \qquad (6h)$$

Propagation

$$\dot{R}_1 + M \xrightarrow{k_{p1}} \dot{R}_2 \qquad (6i)$$
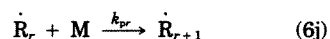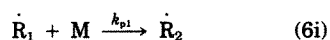
$$\dot{R}_r + M \xrightarrow{k_{pr}} \dot{R}_{r+1} \qquad (6j)$$

In these equations I, M, and S represent initiator, monomer, and solvent (or other substrate), respectively, and P_r stands for a dead polymer molecule containing r monomer units. Subscripts attached to rate coefficients refer to the type of reaction (i,p,f,t_c,t_d), the molecule reacting with the radical (M,S), and

the size of the participating radical. f(eq. 6a) is an efficiency factor defined more precisely in the upcoming section on Idealized Kinetics.

The Stationary State Hypothesis. To derive kinetic expressions from a scheme such as equation 6, it is customary to use the stationary state hypothesis. A stationary state is most usefully defined as a phase of reaction in which the rate of change of radical intermediates is much smaller than their rate of formation or rate of destruction. Let $[\dot{R}]$ be the total propagating radical concentration, so that

$$[\dot{R}] = \sum_r [\dot{R}_r] \qquad (7)$$

If $\mathscr{I}$ is the rate of radical formation and R_d the total rate of radical destruction in the termination reactions (eqs. 6i, 6j), then in the stationary state

$$\frac{d[\dot{R}]}{dt} = \mathscr{I} - R_d \ll \mathscr{I}, R_d \qquad (8)$$

Under these conditions, to a good approximation

$$\frac{d[\dot{R}]}{dt} = \mathscr{I} - R_d = 0 \qquad (9)$$

Equation 9 may be regarded as the formal definition of the stationary state.

Idealized Kinetics. Development of kinetic expressions from the ideal scheme (eqs. 6a–j) is enormously simplified by making certain assumptions. Chief among these are the following: (1) The velocity coefficients are independent of radical size. (2) A stationary state is established for all radical intermediates. (3) The mean kinetic chain length is large. Some important results are given below.

$$R_p \equiv -\frac{d[M]}{dt} = k_p[\dot{R}][M] \qquad (10a)$$

$$= k_p[M]\left(\frac{\mathscr{I}}{k_{t_c} + k_{t_d}}\right)^{1/2} \qquad (10b)$$

$$\overline{P_n} = \frac{\text{rate of consumption of monomer}}{\text{rate of formation of polymer molecules}}$$

$$= \frac{k_p[M][\dot{R}]}{(k_{fM}[M] + k_{fS}[S])[\dot{R}] + (\frac{1}{2}k_{t_c} + k_{t_d})[\dot{R}]^2} \qquad (11)$$

$$= \frac{k_p[M]}{k_{fM}[M] + k_{fS}[S] + \dfrac{(\frac{1}{2}k_{t_c} + k_{t_d})\mathscr{I}^{1/2}}{(k_{t_c} + k_{t_d})^{1/2}}}$$

$$\frac{1}{\overline{P_n}} = \frac{1}{\overline{P_n^0}} + \frac{k_{fS}[S]}{k_p[M]} \qquad (11a)$$

In these equations (which give instantaneous values), R_p is the rate of polymerization, $\mathscr{I}$ is the mean kinetic chain length, and $\overline{P_n}$ the number-average degree of polymerization.

Temperature and Pressure Effects. The influence of temperature on the quantities considered is determined by the acti-

vation energies of the appropriate component reactions. Thus the overall activation energies associated with the rate of polymerization and the mean kinetic chain length, E_0 and E_ν, respectively, are

$$E_0 = \tfrac{1}{2}E_i + E_p - \tfrac{1}{2}E_t$$
$$E_\nu = -\tfrac{1}{2}E_i + E_p - \tfrac{1}{2}E_t \qquad (12)$$

where E_i, E_p, and E_t refer to initiation, propagation, and termination, respectively. E_p and E_t are normally small (~30, ~12 kJ/mol or ~7, ~3 kcal/mol, respectively), so that for thermally initiated reactions, E_i is often the largest (~120 kJ/mol or ~30 kcal/mol). For polymerizations initiated photochemically or by high-energy radiation E_i is close to zero and E_0 is, therefore, much smaller.

Relaxation of Simplifying Approximations. The validity of the assumption that the mean kinetic chain length is large depends on negligible consumption of monomer by reactions other than propagation. When the average kinetic chain length is small, this does not hold and allowance must be made for reaction of monomer in initiation and transfer processes.

A general treatment of free-radical polymerization with no assumptions about the form of the dependence of radical reactivity on chain length is impracticable. The validity of the assumption that the velocity coefficients are independent of radical size was questioned at an early stage, since it seems intuitively unlikely to be true. The propagation reaction would not be expected to be very sensitive to viscosity changes in the normal range encountered up to medium degrees of conversion, since it involves one small and rapidly diffusing species (the monomer).

A different situation prevails for termination, which is much more rapid and involves two macromolecules and which, therefore, might be anticipated to be markedly sensitive to viscosity changes. It is currently supposed that termination is diffusion-controlled; however, viscosity changes arising from polymers in solution have relatively little effect on the rate coefficient, mainly because they influence the macroscopic viscosity of the system, whereas the rates of segmental rearrangement of the interacting chains appear to play a more important role in termination, except in highly viscous systems. The assumption of a constant rate coefficient for termination (in a given solvent) is a reasonable approximation for small to moderate conversions, provided the mean radical size is not too small.

Relaxation of the assumption that a stationary state is established for all radical intermediates does not introduce any new matters of chemical principle, although it may cause greatly increased mathematical complexities. Nonstationary states are most commonly encountered when there is a rapid change in the rate of initiation, as in photochemically initiated reactions when the light is turned on or off or in thermal reactions with a rapidly decaying initiator.

Pre- and Aftereffects. The pre-effect and the aftereffect are the best-known examples of nonstationary processes in free-radical polymerization and may be treated rather simply. For the pre-effect in a system with photochemical initiation, assume a stationary state has been set up with a (low) rate of initiation $\mathcal{J}_1$ and at time $t = 0$ the light intensity is increased instantaneously to give a new rate of initiation $\mathcal{J}_1 + \mathcal{J}_2$. In the nonstationary state that ensues the radical concentration builds up, relatively quickly at first, but subsequently more slowly

until a second stationary state is reached. If the values of the radical concentration in the initial and final stationary states are $[\dot{R}]_1$ and $[\dot{R}]_2$, respectively,

$$[\dot{R}]_1 = \left(\frac{\mathcal{J}_1}{k_t}\right)^{1/2} \qquad [\dot{R}]_2 = \left(\frac{\mathcal{J}_1 + \mathcal{J}_2}{k_t}\right)^{1/2} \qquad (13)$$

For $t \geq 0$ the radical concentration follows equation 14:

$$\frac{d[\dot{R}]}{dt} = \mathcal{J}_1 + \mathcal{J}_2 - k_t[\dot{R}]^2 \qquad (14)$$

integration of which with the boundary condition $[\dot{R}] = [\dot{R}]_1$ at $t = 0$ yields

$$[\dot{R}] = \theta \left(\frac{\mathcal{J}_1}{k_t}\right)^{1/2} \left\{\frac{(\theta + 1)\exp\,[2\theta\mathcal{J}_1^{1/2}k_t^{1/2}t] - \theta + 1}{(\theta + 1)\exp\,[2\theta\mathcal{J}_1^{1/2}k_t^{1/2}t] + \theta - 1}\right\} \qquad (15)$$

In this equation θ is given by

$$\theta = \left(\frac{\mathcal{J}_1 + \mathcal{J}_2}{\mathcal{J}_1}\right)^{1/2} \qquad (16)$$

θ is therefore equal to the ratio of the final to the initial radical concentration or the final to the initial rate of polymerization. The total pre-effect ΔM_{pre} is then

$$\Delta M_{pre} = \frac{k_p[M]}{k_t} \ln \frac{2\theta}{\theta + 1} \qquad (17)$$

The aftereffect may be treated in a completely analogous way by considering the changes in a system, initially in a stationary state with rate of initiation $\mathcal{J}_1 + \mathcal{J}_2$ brought about by reducing the rate of initiation instantaneously at $t = 0$ to $\mathcal{J}_1$. The relation determining the radical concentration at $t \geq 0$ corresponding to equation 14 is

$$\frac{d[\dot{R}]}{dt} = \mathcal{J}_1 - k_t[\dot{R}]^2] \qquad (18)$$

Hence,

$$[\dot{R}] = \left(\frac{\mathcal{J}_1}{k_t}\right)^{1/2} \left\{\frac{(\theta + 1)\exp\,[2\mathcal{J}_1^{1/2}k_t^{1/2}t] + \theta - 1}{(\theta + 1)\exp\,[2\mathcal{J}_1^{1/2}k_t^{1/2}t] - \theta + 1}\right\} \qquad (19)$$

The total aftereffect M_{aft} is then

$$\Delta M_{aft} = k_p[M] \int_0^\infty ([\dot{R}] - [\dot{R}]_2)dt$$

$$= \frac{k_p[M]}{k_t} \ln \frac{\theta + 1}{2} \qquad (20)$$

Other Nonstationary Systems. The behavior of polymerizing systems in which the initiators have relatively short half-lives has been discussed by several authors. Tobolsky remarked that "when fast initiators are used in styrene at moderate temperature the polymerization stops at quite low conversions." This phenomenon was termed dead-end polymerization and attributed to early depletion of the initiator at a stage when appreciable monomer remains unreacted.

Relationships have been derived for polymerization with first- or second-order initiator decay, notably moments of the molar mass distribution, using stationary state treatment. By considering general solutions of equation 21, results also have been developed for first-order initiator decay in which there were no restrictions on the half-lives of the initiator or the kinetic chains:

$$\frac{d[\dot{R}]}{dt} = nk_d[I]_0 e^{-k_d t} - k_t[\dot{R}]^2 \qquad (21)$$

Equation 21 was transformed into the modified Bessel equation (eq. 22):

$$\frac{d^2 y}{du^2} + \frac{1}{u}\frac{dy}{du} - y = 0 \qquad (22)$$

where

$$[\dot{R}] = \frac{1}{k_t y}\frac{dy}{du}$$

$$u = 2\left(\frac{n[I]_0 k_t}{k_d}\right)^{1/2} e^{-k_d t/2} \qquad (23)$$

Hence,

$$[\dot{R}] = -\frac{uk_d}{2k_t}\frac{I_1(u) + \lambda K_1(u)}{I_0(u) + \lambda K_0(u)} \qquad (24)$$

where $I_1(u)$ and $K_1(u)$ are the modified Bessel functions of order one.

Inhibition and Retardation

Kinetics of Ideal Inhibition. Inhibitors and retarders are substances which when added to polymerization reactions in very low concentrations produce large decreases in rate. Mechanisms responsible for this behavior are deactivation of initiating centers or reduction in their rate of generation (inhibitors) and the interruption of propagating chains (retarders). The kinetic behavior of ideal inhibitors and retarders is of interest in that it provides an important method of determining rates of initiation $\mathcal{I}_0$ in polymerization reactions.

The relevant reactions are

$$I \xrightarrow{fk_d} 2\,\dot{R}_0 \qquad (6a)$$

$$\dot{R}_0 + M \xrightarrow{k_i} \dot{R}_1 \qquad (6b)$$

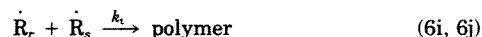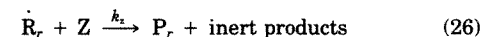$$\dot{R}_0 + Z \xrightarrow{k_z} \text{inactive products} \qquad (25)$$

where Z is the inhibitor and equation 25 is the inhibition process.

The distinction between inhibitors and retarders, although clear in classical chain theory, is generally rather blurred in polymerizations. A single substance may function either as inhibitor or retarder or both, depending on its concentration, so that distinction becomes a matter of degree. In terms of gross behavior, addition of inhibitor effectively brings a polymerization to a stop, whereas addition of a retarder merely reduces the rate.

Ideal inhibitors and retarders destroy active radicals without producing any species capable of reinitiation or further

reaction with radicals. A stable free radical may act in this way. In the ideal kinetics of these systems, therefore, the nature of the bimolecular termination between propagating radicals remains unchanged, although it may be drastically reduced or even eliminated, but there are no interactions between growing chains and species formed in the inhibition or retardation processes.

Kinetics of Ideal Retardation. The reaction scheme for ideal retardation is set out below.

$$I \xrightarrow{fk_d} 2\,\dot{R}_0 \qquad (6a)$$

$$\dot{R}_0 + M \xrightarrow{k_i} \dot{R}_1 \qquad (6b)$$

$$\dot{R}_r + M \xrightarrow{k_p} \dot{R}_{r+1} \qquad (6d)$$

$$\dot{R}_r + Z \xrightarrow{k_z} P_r + \text{inert products} \qquad (26)$$

$$\dot{R}_r + \dot{R}_s \xrightarrow{k_t} \text{polymer} \qquad (6i,\ 6j)$$

Equation 26 represents the retardation reaction and the inert products include a dead polymer P_r. In general, the two termination processes (eq. 26 and eqs. 6i, 6j) occur simultaneously, but if retardation is sufficiently strong, equation 26 will predominate.

Determination of Rates of Initiation

Rates of initiation may be determined by use of inhibitors and retarders, from the mean kinetic chain length, and by use of initiators giving known rates of initiation.

Nonideal Free-radical Polymerization

Departures from the classical relations of free-radical polymerization hitherto discussed may be of two types. First, systems may deviate from thermodynamic ideality, and secondly, additional reactions may participate. A single system may show nonclassical behavior of both types.

Medium Effects. Polymerizations, like other reactions in solution, are subject to medium effects. The assumption often made that solvents which do not participate chemically are merely inert diluents is equivalent to supposing that the polymerization obeys gas-phase kinetics. In fact, the component reactions in polymerization are subject to medium effects similar to those encountered with low-molecular-weight reactions. The rate equations for reactions in solution contain activity coefficients, and unless these are maintained effectively constant, relations involving concentrations can be obscured. Changes in activity coefficients arising from marked differences in properties (eg, polarities) of monomers and solvents, associated with significant deviations from Raoult's law, or from large concentration changes may lead to deviations from simple kinetic relations.

Diffusion Control. The sensitivity of the conformations of macromolecules to the environment introduces important medium influences into polymerizations. Chain termination, which is diffusion-controlled, is particularly sensitive to medium changes. Diffusion control is manifest in two respects, involving diffusion of the whole molecule and segmental diffusion, respectively.
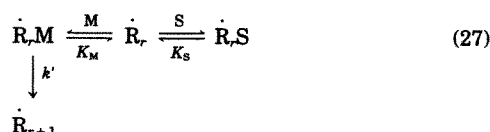
Low polymer concentrations may exert a rather subtle effect. The dimensions of the growing chains may change with increasing (dead) polymer concentration, so that the diffusion

coefficient and hence k_t increase. Thus, the rate of polymerization may fall over the first few percent conversion.

The nature of the solvent also plays an important role in determining polymer coil dimensions and so has a significant influence on k_t. A decrease in the solvent quality for the polymer brings about an increase in k_t and hence decreases the rate of polymerization. Radical size also influences k_t.

Ionization and Enolization. Solvent changes may induce structural modifications in monomers and radicals, for example ionization and enolization, which may greatly influence rates of polymerization. In copolymerization, similar effects may produce changes in the values of reactivity ratios.

Radical Complexation. There has been a considerable discussion of the extent to which polymer radicals can be assumed to be free. It has been pointed out that the electron affinities of typical propagating radicals are similar to those of tetracyanoethylene and chloranil, compounds which form charge-transfer complexes with many of the common solvents used in free-radical polymerization. An early theory assumed complex formation between radicals and monomer or solvent, propagation being confined to monomer-complexed species.
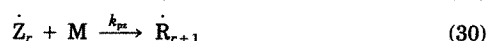
$$\dot{R}_rM \underset{K_M}{\overset{M}{\rightleftharpoons}} \dot{R}_r \underset{K_S}{\overset{S}{\rightleftharpoons}} \dot{R}_rS \qquad (27)$$
$$\downarrow k'$$
$$\dot{R}_{r+1}$$

From equation 27 it follows that

$$-\frac{d[M]}{dt} = k'[\dot{R}M] = k_p[\dot{R}]_t \frac{K_M[M][M]_0}{K_S[S] + K_M[M]} \qquad (28)$$

where $[\dot{R}M]$ is the total concentration of radical–monomer complex, $[\dot{R}]_t$ the total radical concentration, K_M, K_S the equilibrium constants, and k' a rate coefficient. Small solvent effects on k_p have been deduced from rotating-sector measurements in several systems.
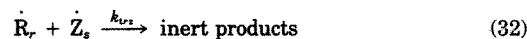
Complex formation between propagating radicals and Lewis acids leads to major changes in reactivity, which are the basis of an important technique for synthesizing alternating copolymers (see COPOLYMERS, ALTERNATING).

Polymerizations with Slow Reinitiation. Complicated situations arise when a retardation product is able to reinitiate only slowly. In an early suggestion, Flory proposed the mechanism set out below. Here slow reinitiation by retarder radicals $\dot{Z}$ is represented by equation 30 and bimolecular termination between retarder radicals by equation 31. These two processes distinguish this mechanism from others previously discussed.

$$I \xrightarrow{fk_d} 2\dot{R}_0 \qquad (6a)$$
$$\dot{R}_0 + M \xrightarrow{k_i} \dot{R}_1 \qquad (6b)$$
$$\dot{R}_r + M \xrightarrow{k_p} \dot{R}_{r+1} \qquad (6d)$$
$$\dot{R}_r + Z \xrightarrow{k_z} \dot{Z}_r \qquad (29)$$
$$\dot{Z}_r + M \xrightarrow{k_{pz}} \dot{R}_{r+1} \qquad (30)$$
$$\dot{Z}_r + \dot{Z}_s \xrightarrow{k_{tzz}} \text{products} \qquad (31)$$

Equation 29 has been written as an addition reaction, but the kinetic results are also valid if it is a transfer.

A more complete analysis has been carried out employing the Flory scheme with addition of the two termination reactions

$$\dot{R}_r + \dot{Z}_s \xrightarrow{k_{trz}} \text{inert products} \qquad (32)$$
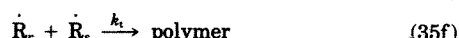$$\dot{R}_r + \dot{R}_s \xrightarrow{k_t} \text{polymer} \qquad (33)$$

Thus all three possible bimolecular termination steps between propagating and retarder radicals are included. The relation (eq. 34) was derived by use of stationary state equations:

$$\frac{\mu^2[Z]}{1-\mu^2}\left[1 + \left\{1 + \frac{1-\mu^2}{\varphi^2\mu^2}\right\}^{1/2}\right]$$
$$= \frac{k_tR_p}{k_pk_z}\left\{1 + \frac{(1-\mu^2)}{\varphi^2\mu^2}\right\}^{1/2} + \frac{k_{pz}k_t[M]}{k_{trz}k_z} \qquad (34)$$

In equation 34 $\mu = R_p/R_p^0$ (ie, the ratio of the rates in the presence and absence of the retarder Z, respectively) and $\varphi = k_{trz}/(k_tk_{tzz})^{1/2}$, a parameter familiar in copolymerization kinetics.

The above treatment has some disadvantages in practice that have limited its general use. Among these is the necessity for a knowledge of R_p^0, the rate of the unretarded polymerization, which cannot always be obtained. To overcome those difficulties, an analysis for a similar scheme was carried out, but without the $\dot{Z} + \dot{Z}$ termination. The complete scheme is given below (eqs. 35). The nomenclature is slightly different from that used originally to make it more compatible with the preceding discussion, but S, representing a retarding solvent, replaces Z, used above for a retarder.

$$I \longrightarrow \dot{R}_0 \qquad (35a)$$
$$\dot{R}_r + M \xrightarrow{k_i} \dot{R}_1 \qquad (35b)$$
$$\dot{R}_r + M \xrightarrow{k_p} \dot{R}_{r+1} \qquad (35c)$$
$$\dot{R}_r + S \xrightarrow{k_s} (P_r +)\dot{S} \qquad (35d)$$
$$\dot{S} + M \xrightarrow{k_{sm}} \dot{R}_1 \qquad (35e)$$
$$\dot{R}_r + \dot{R}_s \xrightarrow{k_t} \text{polymer} \qquad (35f)$$
$$\dot{R}_r + \dot{S} \xrightarrow{k_{trs}} P_r \qquad (35g)$$
$$\dot{S} + \dot{S} \xrightarrow{k_{ss}} \text{inactive products} \qquad (35h)$$

The parentheses apply to degradative addition in which no nonradical polymer is formed. The stationary state treatment with omission of equation 35h leads to the relation (eq. 36)

$$\frac{b}{a^3}R_p^3 + \left(1 + 2abc\frac{[S]}{[M]}\right)\frac{R_p^2}{a^2} - \frac{b\mathcal{F}}{a}R_p - \mathcal{F} = 0 \qquad (36)$$

In this equation

$$a = k_p[M]/k_t^{1/2}; \qquad b = k_{trs}/(k_{sm}k_t^{1/2}[M]); \qquad c = k_z/k_p \qquad (37)$$

The dimensionless quantity

$$abc = \frac{k_{trs}k_z}{k_{sm}k_t} \equiv \mathcal{R} \qquad (38)$$

which determines the extent of retardation and enters into

many kinetic relationships, has been called the intrinsic retardation of the system.

Degradative Reactions Involving Monomer. The formal kinetics of a retarded polymerization do not depend on the nature of the retardation step, both chain transfer and addition giving the same relationships, but when approximations have to be made to obtain tractable expressions, significant differences may appear.

The polymerization of 1-vinylimidazole (VIM) in ethanol solution has been studied. This polymerization is markedly nonclassical; for a given initiator concentration, the order of the rate of polymerization in monomer concentration decreases with increasing $[M]$, tending towards zero at high $[M]$. Such behavior is characteristic of retardation by monomer. Propagating radicals attack the 2-position of the monomer; introduction of a methyl substituent in this position completely removes the retardation, the rate of polymerization of 2-methyl-1-vinylimidazole in ethanol at 70°C being directly proportional to the monomer concentration. Evidence from polymer molar masses suggest that the retardation process consists of addition of propagating chains to the 2-position (rather than hydrogen abstraction) with formation of a relatively unreactive radical $\dot{Z}$:

$$(39)$$
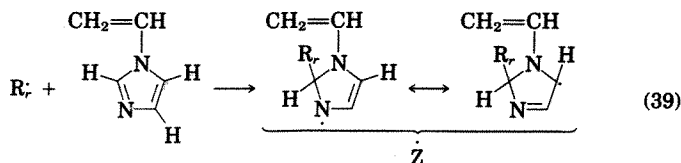
This type of process has been termed degradative addition.

The Kinetics of Polymerization with Degradative Addition. Complete kinetic analysis of a retarded polymerization including three possible termination reactions suffers from some practical disadvantages. Omission of the interactions between retarder radicals ($\dot{Z}$ or $\dot{S}$) produces considerable simplification, but it becomes necessary to examine *a posteriori* to what degree results obtained justify the approximation. It has been shown that the ratio $[\dot{S}]/[\dot{R}]$ (or $[\dot{Z}]/[\dot{R}]$) is inversely proportional to $\lambda = k_{trs}/k_t$. Two cases of interest are distinguished.

1. If $\lambda \sim 1$, the concentration of $\dot{S}$ is not negligible and may exceed that of $\dot{R}$. Neglect of the $\dot{S} + \dot{S}$ termination can therefore only be justified in terms of a sufficiently small k_{tss}.

2. If $\lambda \gg 1$, $[\dot{S}]$ is relatively small, and the $\dot{S} + \dot{S}$ termination is negligible unless k_{tss} is unexpectedly large.

The simplest assumption to make is that in degradative addition polymerizations $k_t = k_{trs} = k_{tss} = k_t'$ with all three reactions being diffusion-controlled. Since these involve polymer chains of identical type (with different terminal groups), the assumed equality is all the more plausible.

Primary Radical Termination. In addition to geminate recombination, a primary radical derived from an initiator is confronted by several possibilities. It may interact with a monomer to form a propagating radical (eq. 2) or it may enter into pri-

mary radical termination by interacting with a growing chain or with a second primary radical. Often primary radical termination is negligible because the radicals are rapidly scavenged by the monomer, but in some circumstances it becomes significant and leads to deviations from ideal kinetic behavior. Deviations are favored by very high rates of initiation and/or low monomer concentrations, since these conditions correspond to a relatively high concentration of primary radicals. Similarly, when the monomer or the primary radical is relatively unreactive, primary termination may become significant.

The qualitative effects of primary termination on polymerization kinetics are easily predictable. The true rate of initiation of propagating chains is no longer proportional to the initiator concentration, but falls progressively below this with increasing concentration so that the initiator exponent falls below 0.5. Further, the rate of initiation becomes dependent on monomer concentration, and the rate of polymerization becomes proportional to a power of [monomer] exceeding one. In the limiting (but practically very improbable) case when all propagating chains end by primary radical termination, the initiator and monomer exponents become zero and two, respectively.

Chemistry of the Component Reactions

Initiation. Polymerization of a reactive vinyl monomer is initiated by free radicals having sufficiently high activity. These may be generated from initiators in diverse ways, among which thermal or photochemical intramolecular bond cleavage, redox reactions, and photochemical hydrogen abstraction are the commonest, but other processes such as use of γ-radiation or electron beams find applications. Initiators belonging to the first group are discussed here, principally (see also ELECTROCHEMICAL INITIATION; PHOTOPOLYMERIZATION).

Thermal Initiators: Intramolecular Bond Cleavage. Nonaqueous Solutions. Azo initiators have a long history in polymer technology (see AZO COMPOUNDS). Since nitrogen is evolved on decomposition they have been used in Germany as blowing agents (qv) in the preparation of lightweight plastics and rubbers.

Most of the compounds are represented by the formula
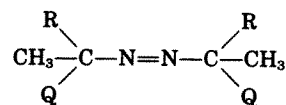
where R = alkyl and Q is a simple carboxylic acid residue or a derivative (nitrile, ester). Azobisisobutyronitrile (AIBN) (R = CH_3, Q = CN) is very widely used as an initiator; 4,4'-azo-4-cyanopentanoic acid (R = CH_3, Q = $(CH_2)_2COOH$) has rather similar initiating properties and, unlike AIBN, is soluble in water.

Thermal decomposition of AIBN and its analogues is generally considered to produce cyanoisopropyl radicals (or analogues) according to
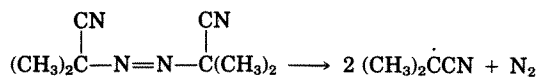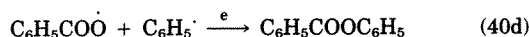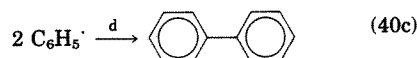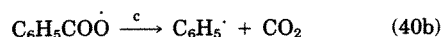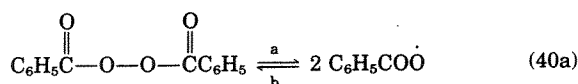

The transient existence of the $(CH_3)_2CN_2\cdot$ radical has been suggested on the basis of esr observations, so that cleavage of
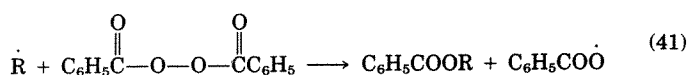
the two C—N bonds may occur consecutively rather than simultaneously.

Peroxy compound chemistry, including decomposition, has been reviewed (see PEROXY COMPOUNDS).

Benzoyl peroxide is a well-established initiator of polymerization, and its reactions have been extensively studied. As with other peroxides, the primary step in the thermal decomposition is scission of the —O—O— bond (eq. 40a) to give two acyloxy radicals. A number of secondary processes may follow; in addition to reacting with monomer, benzoyloxy radicals may recombine (eq. 40b) or undergo β-scission to phenyl radicals and carbon dioxide (eq. 40c). Further recombination reactions giving biphenyl (eq. 40d) and phenyl benzoate (eq. 40e) may then occur.
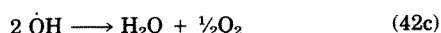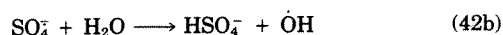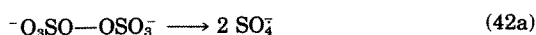
$$C_6H_5\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}C_6H_5 \underset{b}{\overset{a}{\rightleftharpoons}} 2\ C_6H_5C\dot{O}O \qquad (40a)$$

$$C_6H_5C\dot{O}O \overset{c}{\longrightarrow} C_6H_5\dot{} + CO_2 \qquad (40b)$$

$$2\ C_6H_5\dot{} \overset{d}{\longrightarrow} \langle\bigcirc\rangle-\langle\bigcirc\rangle \qquad (40c)$$

$$C_6H_5C\dot{O}O + C_6H_5\dot{} \overset{e}{\longrightarrow} C_6H_5COOC_6H_5 \qquad (40d)$$

Induced decomposition is an important part of the reaction with many peroxides. This is the interaction with any radical $\dot{R}$ present in the system:

$$\dot{R} + C_6H_5\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow C_6H_5COOR + C_6H_5C\dot{O}O \qquad (41)$$

$\dot{R}$ may be phenyl, but since benzoyloxy radicals are active in hydrogen abstraction, many different radicals may arise through interaction with the solvent.

Peresters, which are structurally intermediate between diacyl and dialkyl peroxides, have also received attention as initiators.

Aqueous Solutions. Potassium persulfate is a commonly used initiator in aqueous solution: it has long been employed as an initiator in emulsion polymerization, eg, in the original GR-S (styrene–butadiene synthetic rubber) recipe. ("Activated" recipes, in which ferrous salts are added to form redox systems, are also used.) The following reaction scheme (eqs. 42) for the thermal decomposition of persulfate in neutral and alkaline solutions, has been proposed.
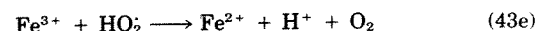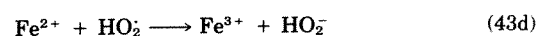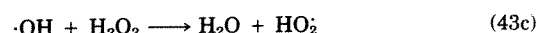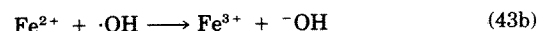
$$^-O_3SO-OSO_3^- \longrightarrow 2\ SO_4^- \qquad (42a)$$

$$SO_4^- + H_2O \longrightarrow HSO_4^- + \dot{O}H \qquad (42b)$$

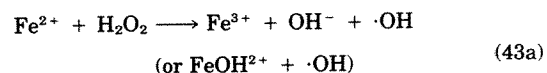$$2\ \dot{O}H \longrightarrow H_2O + \tfrac{1}{2}O_2 \qquad (42c)$$

Redox Initiators. The discovery in 1940 that addition of small quantities of reducing agents to peroxides greatly accelerates radical generation opened the important field of redox initiation. Redox initiators, systems based on mixtures of oxidizing and reducing agents, have acquired great importance, particularly in industry, eg, in low-temperature emulsion polymerization. They initiate through the occurrence of one-electron

transfer steps that form free-radical intermediates. Free-radical polymerization has been used in the elucidation of many redox mechanisms, as for example in the much-studied system ferrous ion plus hydrogen peroxide (Fenton's reagent), since it provides a demonstration of the intervention of free radicals and allows their rate of formation to be measured. Many redox initiators are known and numerous "recipes" are current in emulsion polymerization technology.

Redox initiators may be classified according to their solubilities (in water or organic liquids) or their mode of radical generation.

Aqueous Redox Initiators Forming Single Radicals. The powerfully oxidizing properties of mixtures of hydrogen peroxide and ferrous salts, discovered by Fenton in 1894, have been attributed to the participation of $\dot{O}H$ and $\dot{H}O_2$ radicals. Later work has largely confirmed that view and scheme 43 for the principal component reactions is now accepted.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \cdot OH$$
$$(\text{or } FeOH^{2+} + \cdot OH) \qquad (43a)$$

$$Fe^{2+} + \cdot OH \longrightarrow Fe^{3+} + {}^-OH \qquad (43b)$$

$$\cdot OH + H_2O_2 \longrightarrow H_2O + H\dot{O}_2 \qquad (43c)$$

$$Fe^{2+} + H\dot{O}_2 \longrightarrow Fe^{3+} + HO_2^- \qquad (43d)$$

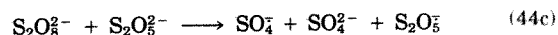$$Fe^{3+} + H\dot{O}_2 \longrightarrow Fe^{2+} + H^+ + O_2 \qquad (43e)$$

Organic peroxides or persalts such as potassium persulfate can enter into similar reactions, which are essentially one-electron transfers with concomitant cleavage of the —O—O— bond.

Other transition metal ions such as Ti^{3+} can enter into similar reactions.

Aqueous Redox Initiators Forming Pairs of Radicals. Systems in which two relatively stable salts form a redox pair are commonly used in industrial emulsion polymerizations. Typical oxidizing agents are potassium persulfate, potassium ferricyanide, ceric sulfate, potassium permanganate, t-butyl hydroperoxide, cumene hydroperoxide, pinane hydroperoxide, and diisopropylbenzene hydroperoxide. Reducing agents include sodium hyposulfite, sodium metabisulfite, sodium sulfide, sodium thiosulfate, and hydrazine hydrate. No transition metal derivatives are included in these examples. Both oxidizing and reducing components form free radicals, which, in principle, may initiate polymerization, although the behavior in any given system depends on the radical and monomer reactivities.

Typical redox processes in this class, the interactions of cumene hydroperoxide with thiosulfates and of persulfates with thiosulfates and metabisulfites, are shown in equations 44.

$$\underset{(CH_3)_2\overset{C_6H_5}{\overset{|}{C}}OOH}{} + S_2O_3^{2-} \longrightarrow (CH_3)_2\overset{C_6H_5}{\overset{|}{C}}O\cdot + S_2O_3^- + {}^-OH \qquad (44a)$$

$$S_2O_8^{2-} + S_2O_3^{2-} \longrightarrow SO_4^- + SO_4^{2-} + S_2O_3^- \qquad (44b)$$

$$S_2O_8^{2-} + S_2O_5^{2-} \longrightarrow SO_4^- + SO_4^{2-} + S_2O_5^- \qquad (44c)$$
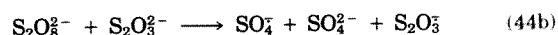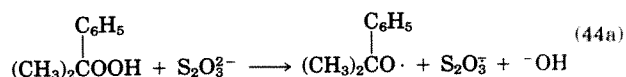
Nonaqueous Redox Initiators. Organic peroxides may react in nonaqueous solution by redox processes. It has long been known that benzoyl peroxide can enter into relatively rapid reactions with primary, secondary, and tertiary amines.

The most familiar systems include diacyl peroxides and ter-

tiary amines, of which benzoyl peroxide and dimethylaniline are typical. The reactants form a complex which cleaves into radicals:

$$C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}} + C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5 \longrightarrow$$

$$\left[C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}}-OOCC_6H_5 \quad C_6H_5COO^- \right] \longrightarrow$$

$$\text{complex}$$

$$C_6H_5\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\,\cdot\,+}}} + C_6H_5\overset{\displaystyle \cdot}{C}OO + C_6H_5COO^- \quad (45)$$

$$\underbrace{\hspace{5cm}}_{(3)}$$
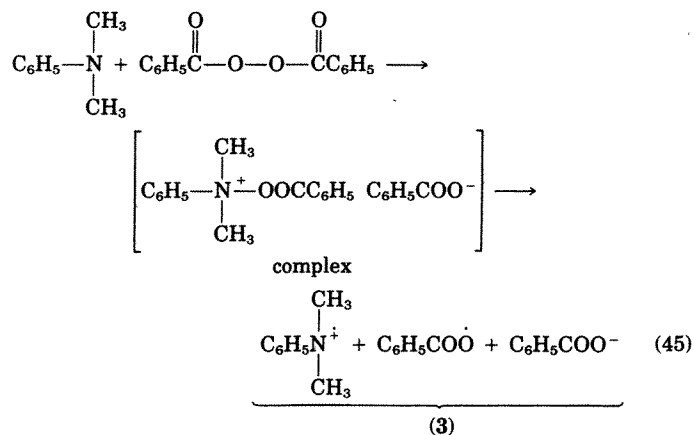
In the absence of monomer further reactions occur:

$$(3) \longrightarrow C_6H_5COOH + C_6H_5\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2OOCC_6H_5}{|}}{N}} \xrightarrow{\ H_2O\ }$$

$$C_6H_5NHCH_3 + CH_2O + C_6H_5COOH \quad (46)$$

$$(3) \longrightarrow C_6H_5COO-\!\!\!\bigcirc\!\!\!-N(CH_3)_2 + C_6H_5COOH$$

Decomposition is accelerated by electron-donating substituents in the dimethylaniline and retarded by electron withdrawal. Electron-withdrawing groups in the peroxide accelerate the reaction. These observations all support the occurrence of complex formation.

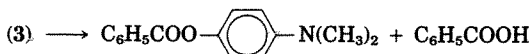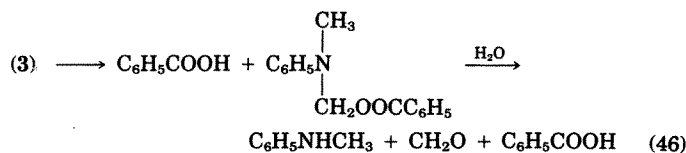*Initiators Based on Transition Metal Derivatives.* Transition metal derivatives with the metal atoms in a low (preferably zeroth) oxidation state may function as components of initiating systems in two distinct ways. Both require the presence of a coinitiator; in type 1 the coinitiator is an organic halide (see below) and in type 2 it is an olefin carrying electron-attracting groups or acetylene or an acetylene derivative. Both types of systems are active as thermal and photoinitiators. Systems of type 2 have so far been used mainly as photoinitiators and will be discussed later.

Transition Metal Derivative plus Organic Halide Initiators. In 1959 the use of metal carbonyls in the presence of high concentration of carbon tetrachloride in the synthesis of ethylene telomers was reported. It was found that although the carbonyls alone are not initiators, they and many other transition metal derivatives become active free-radical sources in the presence of low concentrations of organic halides. An extensive study has been made of these initiators.

Nonaqueous Redox Initiators. Intramolecular Processes. Metal chelates have attracted considerable attention as initiators and appear to be able to initiate different types of polymerizations according to the conditions. Cationic or coordinated cationic polymerization initiated by acetylacetonates (particularly $MoO_2(acac)_2$) has been reported; $Mn(II)(acac)_2$ and $Co(II)(acac)_2$ bring about the polymerization of chloral at room temperatures, probably by a coordinated anionic mechanism. Some chelates produce radicals on heating. Further, several chelates initiate polymerization of styrene and other vinyl monomers

on heating. The following order of rates of polymerization has been given.

$$V(III) < Cr(III) = Al(III) < Fe(III) < Co(III) < Ce(IV) < Mn(III)$$

In all the chelate reactions discussed, the initiating radicals are derived from the ligands, so that the processes can be used for incorporating such groups into the terminal positions in polymer chains.

Photoinitiators. Polymerization may be initiated by high- or low-energy radiation. γ-Rays from ^{60}Co or high-energy electrons may initiate ionic polymerization in special circumstances, notably at low temperatures with ultrapure monomers in media of high dielectric constant. High-energy irradiation commonly initiates free-radical polymerization and is much employed for the synthesis of graft copolymers (see GRAFT COPOLYMERS).

Initiation by low-energy radiation, visible or ultraviolet light, will be discussed here. Apart from its value in mechanistic studies, photoinitiation is the basis of important commercial processes including microlithography and photocuring. These processes rely on the cross-linking of multifunctional monomers by free-radical or cationic reactions (see PHOTOCHEMISTRY; PHOTOPOLYMERIZATION; LITHOGRAPHIC RESISTS). Note that photoinitiated polymerization is to be distinguished from photopolymerization, in which each propagation step is effected by the radiation.

Photoinitiators for free-radical polymerization fall into two classes: those which on irradiation undergo intramolecular bond cleavage leading to radical generation and those which when photoexcited abstract hydrogen atoms from H-donors and so form radicals. Among the former are azo compounds (eg, azobisisobutyronitrile), peroxides (eg, benzoyl peroxide), and aliphatic carbonyl compounds (ketones and diketones). The latter group includes aromatic ketones such as benzophenone and derivatives.

Photosensitized Initiation: Polymeric Photosensitizers and Photoinitiators. In a photosensitized reaction, light is absorbed by the photosensitizer and the excitation energy is transferred to an acceptor molecule which subsequently reacts. The photosensitizer is not chemically changed in the process (although, of course, accompanying reactions may result in its decomposition). Photosensitization by excited triplet species, such as the (n,π^*) and (π,π^*) triplets of aromatic ketones and hydrocarbons, respectively, is particularly well documented (see PHOTOCHEMISTRY). These processes are, of course, quite distinct from the hydrogen abstraction reactions discussed in the preceding section, in which the molecule photoexcited by light absorption reacts chemically with another species.

Polymeric photosensitizers and photoinitiators have been described. Many of these are polymers based on benzophenone, eg, poly(p-divinylbenzophenone) (DVBP). Such rigid polymers are reported to be effective sensitizers since hydrogen abstraction from the backbone by excited benzophenone is less likely.

Photoinitiators have been developed in which different types of photoinitiating functionality are combined in one molecule, for example, peresters of the type

$$R-\!\!\bigcirc\!\!-\overset{\overset{\displaystyle O}{\|}}{C}-\!\!\bigcirc\!\!-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-t\text{-}C_4H_9$$

$$(4)$$
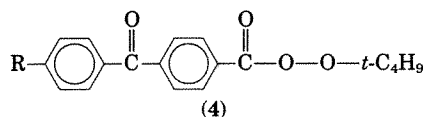
where R = CH_3, CH_3O, $BrCH_2$, t-C_4H_9O—O—$\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}$, and also the peroxide
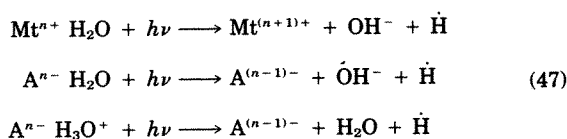

(5)
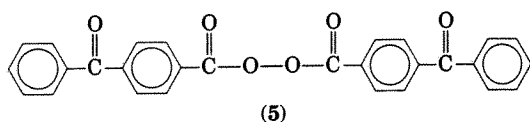
In other systems, the benzophenone chromophore is replaced by (π,π^*) absorbers such as fluorenone, anthracene, and pyrene. When irradiated by light of $\lambda = 366$ nm, benzophenone derivatives (4) (R = H) and (5) initiate free-radical polymerization with effectively classical kinetic features ($R_p \alpha [M],[I]^{1/2}$) at low monomer and initiator concentrations. Polymers prepared from these initiators carry benzophenone end groups.

Redox-type Photoinitiators. Aqueous systems based on metal ion reactions and photoinitiation by dyes and by transition metal derivatives are now discussed.

From a study of the photodecomposition of water in the hydration shells of metal cations Mt^{n+} and anions A^{n-} it was concluded that hydrogen atoms are generated and can initiate polymerization (eq. 47).

$$Mt^{n+} \; H_2O + h\nu \longrightarrow Mt^{(n+1)+} + OH^- + \dot{H}$$

$$A^{n-} \; H_2O + h\nu \longrightarrow A^{(n-1)-} + \dot{O}H^- + \dot{H} \qquad (47)$$

$$A^{n-} \; H_3O^+ + h\nu \longrightarrow A^{(n-1)-} + H_2O + \dot{H}$$

In some systems (eg, with cuprous ions) complex formation between monomer and ions interfered with initiation.

Many ion pairs have been shown to photoinitiate, including $Fe^{3+}OH^-$, $Fe^{3+}Cl^-$, $Fe^{3+}F^-$, $Fe^{3+}N_3^-$, $Fe^{3+}C_2O_4^{2-}$, $Fe^{3+}H$ citrate^{2-}, $Pb^{2+}Cl^-$, $Ce^{4+}OH^-$, $Co^{3+}(H_2O)_6(NO_3)_3$; and electron transfer may involve the ligand (eq. 48).

$$Fe^{3+}X^- + h\nu \longrightarrow Fe^{2+}\dot{X} \longrightarrow Fe^{2+} + \dot{X} \qquad (48)$$
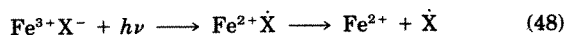
Dye-sensitized photoinitiation is of practical interest in rapid imaging processes for displays and holography. One familiar system employs aqueous solutions of barium acrylate or acrylamide with a photoredox pair composed of a phenothiazine dye and benzene sulfinate ions.

Photoinitiation by Transition Metal Derivatives. Many transition metal derivatives of the types discussed (eg, carbonyls) photoinitiate free-radical polymerization in the presence of organic halides. Early observations have been described and possible reaction mechanisms outlined. It seems likely that all these reactions are basically similar to the type 1 thermal initiation already described.

Manganese and rhenium carbonyls are probably among the most useful photoinitiators of this group. The long-wave limits of absorption are approximately 460 and 380 nm, respectively, and photoinitiation occurs up to these wavelengths. Manganese carbonyl is therefore active in visible light. Quantum yields are of the order unity.

Recognition of type 2 photoinitiation started with the observation that pure liquid tetrafluoroethylene at $-93°C$ containing a low concentration of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ polymerizes rapidly when irradiated. It was concluded that the reaction is a free-radical polymerization, with C_2F_4 acting as coinitiator to form initiating radicals of type $(CO)_5MnCF_2CF_2$.

Efficiency of Initiation. The initiator efficiency f was introduced to accommodate the experimental observation that the rate of initiation is often less than anticipated from a knowledge of the rate of dissociation of the initiator $k_d[I]$. Here k_d refers only to the primary dissociation and not to the total decomposition, which may include induced decomposition (as, for example, with diacyl peroxides). If each molecule dissociates into n primary radicals, the efficiency of initiation is defined by equation 49.

$$f = \frac{\mathcal{J}}{nk_d[I]} \qquad (49)$$

Values of f less than unity may arise from partial decomposition into noninitiating products or from participation of the primary radicals in "wastage" (ie, noninitiating) processes. Primary radical termination and reaction of primary radicals with inhibitors are wastage reactions; these have already been considered and are not included in the present discussion.

Many common initiators have efficiencies in the range 0.3–0.8; azobisisobutyronitrile, for example, has $f \sim 0.6$ over a wide range of monomer concentrations. It is generally agreed that these low efficiencies are often the result of cage phenomena. A pair of primary radicals formed in a solvent cage is confronted by several possibilities: (1) mutual interaction and destruction, (2) reaction of one (or both) radicals with a species (eg, monomer or solvent) in the walls of the cage, (3) diffusion out of the cage into the body of the solution. Of these, (1) does not lead to chain initiation; the process is conveniently described as geminate interaction, signifying that the partners originate from a single molecule. If the interaction (1) is a simple recombination, the parent molecule is reformed and the process, which is obviously without overall chemical effect, does not contribute to radical wastage and reduce f. On the other hand, if (1) yields a noninitiating species or an initiator of lower activity, it represents a wasteful process which decreases the efficiency of initiation. Clearly, if radical generation is accompanied by the simultaneous elimination of a stable small molecule such as N_2 or CO_2, geminate recombination cannot reform the parent molecule.

Reactions Between Primary Radicals and Monomers. The relative rates and regioselectivities of addition and transfer reactions of free radicals are matters of central importance in free-radical polymerization. This section deals with addition and hydrogen-abstraction reactions between primary radicals and monomers.

It was long assumed that primary radicals react with monomers almost exclusively by addition, normally to the tail-end of the double bond. Developments in spin-trapping and esr techniques have greatly facilitated experimental investigations, and it turns out that the above hypothesis is broadly applicable, although important deviations have come to light.

More recent and detailed work reveals some complications that can be encountered, especially with oxygen-centered radicals. Practical consequences arising from the introduction of defect groups into polymers through the initiation process have been discussed.

Initiation by t-butoxy radicals generated by thermal decomposition of di-t-butyl peroxalate has received considerable attention. Decomposition of di-t-butyl peroxalate (0.02 mol/dm^3) at 60°C in methyl methacrylate in ˙ ˚ presence of the spin-

trap 1,1,3,3-tetramethylisoindoline-2-oxyl (0.044 mol/dm³) yields six products which may be translated into the reaction pathways summarized in scheme 50. The expected tail addition to monomer forming radical (7) accounts for only 63% of the total. Hydrogen abstraction from both methyl groups occurs, that · from the allylic position giving (8) (29%) and that from the ester methyl forming (6) (4%). This result is of practical importance since the structure and properties of the final polymer

can be influenced by the nature of the initiating radicals. Thus (8) may be incorporated as an unsaturated terminal group by initiation (a fairly probable process) or by combination with a growing chain; radical (6) has been shown to initiate and would also form unsaturated end groups. It is well known that such groups have a deleterious influence on polymer stability; they also increase the possibility of branching during polymerization since the polymer molecule behaves as a macromer. Hydrogen abstraction from the ester moiety increases in importance with the size of the alkyl group.

(50)
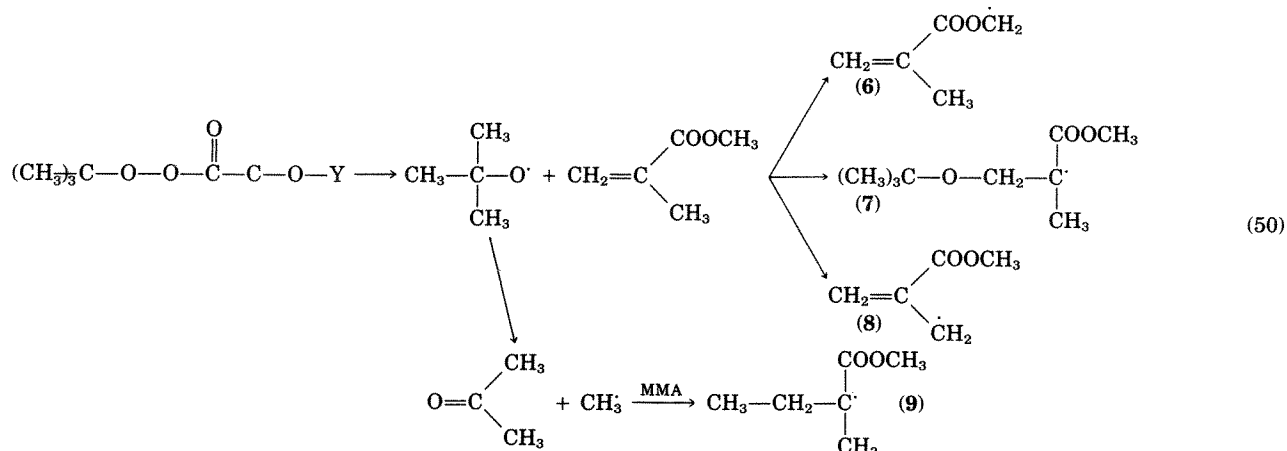
Solvent effects on reactions of t-butoxy radicals with methyl methacrylate have been investigated, and the importance of hydrogen abstraction relative to addition increases with increasing solvent polarity. A greater degree of charge separation may exist in the transition state for hydrogen abstraction or the relative rates may be influenced by interaction of the solvation shells of the reactants. The latter would lead to the observed result if addition were more sterically demanding. The solvent effect clearly has implications in commercial polymer preparation.

Rates of addition of radicals to double bonds are dependent on several parameters, among which polar and steric factors, stabilization of the radical products, and strengths of bonds being formed and broken all play a part. These are discussed more fully later under Propagation.

In an interesting study of the regioselectivity of free-radical processes, reactions of the three electrophilic radicals benzoyloxy, phenyl, and t-butoxy with the three α–β unsaturated esters (monomers) methyl acrylate, methyl methacrylate, and methyl crotonate were examined. For the three monomers, the ratio of hydrogen abstraction to double bond addition increased in the series benzoyloxy < phenyl < t-butoxy, and the ratio of head-to-tail addition decreased in the same series. Relative rates of head and tail addition were determined by competition experiments, the initiator being decomposed in a mixture of

methyl acrylate, methyl methacrylate, and methyl crotonate. Results are presented in Table 1 together with data for cyclohexyl radicals.

The overall rates of addition of radicals to various monomers, collected from various sources, presented in Table 2, illustrate the influence of polar factors.

Spontaneous Thermal Polymerization. A few very highly purified monomers, of which styrene is the best-known example, undergo genuine thermal polymerization in the absence of added initiators. These reactions are uncommon and normally very slow, so that they are highly sensitive to traces of inhibitors or initiators and their existence is not easy to establish. A summary has been given. The mechanism of initiation in the thermal polymerization of styrene has been the subject of much debate. Mayo observed that the rate of initiation is third-order in styrene and that low molecular weight products are also formed. He suggested that radical generation involves formation of a Diels-Alder dimer, which subsequently reacts with styrene.

Strong confirmatory evidence of the correctness of Mayo's proposal has recently been reported, based on the analysis of ¹H nmr spectra of styrene oligomers composed of 6–14 units, prepared by thermal polymerization in the presence of ferric chloride as ideal retarder (see OLIGOMERS).

Table 1. Relative Rate Coefficients for Tail and Head Addition of Radicals (k_T, k_H, respectively) to Acrylate Monomers at 60°C

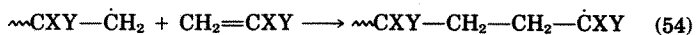| Monomer	$C_6H_5COO\cdot$		$C_6H_5\cdot$		$(CH_3)_3C\dot{O}$		$C_6H_{11}\cdot$	
	k_T	k_H	k_T	k_H	k_T	k_H	k_T	k_H
methyl acrylate	1.0	0.2	1.0	0.03	1.0	0.02	1.0	0.002
methyl methacrylate	4.5	0.35	1.6	≤0.01	2.9	0.0	0.71	≤0.001
methyl crotonate	1.3	1.6	0.12	0.07	0.3	≤0.03	0.011	0.001

Table 2. Reactivities of Monomers Toward Radicals

Radical	Temperature, °C	Relative reactivities		
		St	MMA	MAN
cyanoisopropyl	60	1	0.56	0.34
polyMAN·	60	1	0.25	0.16
benzoyloxy	60	1	0.12	
benzoylthiyl	20	1	0.12	
t-butoxy	20	1	0.06	0.03
methyl	65	1	1.82	2.68
phenyl	60	1	1.78	2.46

Propagation. The propagation or growth reaction is the basic polymer-forming process. Considerations of polymer structures and stabilities and reaction mechanisms are all facets of chain propagation. Three aspects are discussed here: propagating radical–monomer reactions, the stereochemistry of propagation and polymer microstructures, and the thermodynamics of polymerization and depropagation.

Rates and Regioselectivity of Propagating Radical–Monomer Reactions. The characteristics of chain propagation are essentially similar to those of primary radical additions to monomer. Structure features determining rates and regioselectivity of addition are of prime concern.

The alternatives of head and tail addition to vinyl monomers lead to the four possibilities in propagation shown in equations 51–54.

$$\text{\small{$\sim$}}CH_2\text{---}\dot{C}XY + CH_2{=}CXY \longrightarrow \text{\small{$\sim$}}CH_2\text{---}CXY\text{---}CH_2\text{---}\dot{C}XY \quad (51)$$

$$\text{\small{$\sim$}}CH_2\text{---}\dot{C}XY + CXY{=}CH_2 \longrightarrow \text{\small{$\sim$}}CH_2\text{---}CXY\text{---}CXY\text{---}\dot{C}H_2 \quad (52)$$

$$\text{\small{$\sim$}}CXY\text{---}\dot{C}H_2 + CXY{=}CH_2 \longrightarrow \text{\small{$\sim$}}CXY\text{---}CH_2\text{---}CXY\text{---}\dot{C}H_2 \quad (53)$$

$$\text{\small{$\sim$}}CXY\text{---}\dot{C}H_2 + CH_2{=}CXY \longrightarrow \text{\small{$\sim$}}CXY\text{---}CH_2\text{---}CH_2\text{---}\dot{C}XY \quad (54)$$
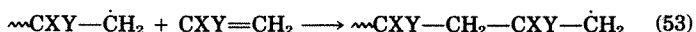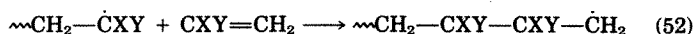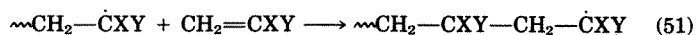
Exclusive propagation by reaction 51 or 53 would lead to polymers of regular head-to-tail structure, whereas reactions 52 and 54 would produce head-to-head and tail-to-tail units. The detailed structure of the polymer chain is determined by the relative rates of the four reactions.

There is compelling experimental evidence from electron spin resonance studies that equation 53 is the major propagation reaction.

Polymers with exclusive head-to-tail addition have been termed "isoregic"; those with half of the units reversed, "syndioregic"; and those with a random arrangement of reversed units, "aregic."

Equally important with regioselectivity are the rates of addition of propagating radicals to monomer. Both are dependent on the same structural features in the radical and monomer and they cannot profitably be discussed separately. From information provided by small-radical studies, important general features may be identified: (1) stabilization of radical reactants and products by electron delocalization, (2) steric effects, (3) polar effects, and (4) the strength of the bond being formed. Combinations of these are usually required to rationalize the experimental data and quantitative treatment has so far not been satisfactory. The strength of the new bond (4) is a function of (1), (2), and (3). Specific influences, such as the presence of

halogen substituents (which lead to weaker bonds), also operate, but they are less common in polymerization since addition to the substituted carbon atoms is exceptional. Its occasional occurrence may be practically important in introducing weak links into the chains.

Free-radical additions are normally facile and exothermic so that according to the Hammond postulate, the transition states are likely to be "early," i.e. to involve little electron and atom redistribution compared to slower processes. The transition states therefore tend to resemble the reactants rather than the products with respect to bond lengths and angles. This is consistent with the small value of the secondary kinetic isotope effects observed when the olefin is substituted with deuterium at the reaction center. Steric and polar interactions, (2) and (3), respectively, between radical and olefin would therefore be expected to be decisive and the influence of stability of the addend radical of less importance.

Wrong-way Additions. Although the interplay of factors (1)–(4) that determines the nature of the propagation reaction results in predominantly head-to-tail addition, "wrong-way" additions in polymer chains are well known. In 1948 Flory and Leutner demonstrated chemically the existence of 1,2-glycol units in poly(vinyl alcohol) prepared by hydrolysis of poly(vinyl acetate) and estimated that the polymer contained about 1% of these units. Thus in the polymerization of vinyl acetate approximately 1% of the additions follow equation 52 to give head-to-head groupings. More recently nmr studies have produced ample evidence for the existence of head-to-head units in polymers. Poly(vinyl fluoride), poly(vinylidene fluoride), and their copolymers have received considerable attention; all have been found to contain such units, and in poly(vinylidene fluoride) it has been estimated that 3.5–6% of the monomer units in the chain are reversed (depending on synthesis conditions) (see HEAD-TO-HEAD POLYMERS; VINYL FLUORIDE POLYMERS; VINYLIDENE FLUORIDE POLYMERS).

Lewis Acid Complexes. Complex formation between reacting species and Lewis acids, generally through interaction with side chains carrying groups such as ester or nitrile, can lead to large changes in the reactivities of radicals and monomers which are the basis of an important general method for synthesizing strongly alternating copolymers.

Stereochemistry of Propagation: Polymer Microstructures. The substituted carbon atom of a monomer unit in a polymer chain is a chiral center (unless it is situated at the precise midpoint of a chain) and therefore has a d or l configuration, depending on the stereochemistry of addition. The assembly of configurations determines the chain microstructure (see MICROSTRUCTURE).

The fine structure of a polymer chain provides a time se-

quence of the propagation steps by which the chain was formed, and a main concern is to relate microstructure to the stereochemistry of propagation. The sequence of propagation reactions is generally considered in terms of Bernoulli trial or Markov statistics.

Thermodynamics of Polymerization. The Depropagation Reaction. Enthalpy and entropy changes in the propagation reaction are, for long chains, effectively those of the overall polymerization (ΔH_p, ΔS_p respectively for the prevailing experimental conditions). Both are negative, so that the free-energy change,

$$\Delta G_p = \Delta H_p - T\Delta S_p \qquad (55)$$

which is negative for a polymerizing system, becomes less negative as the temperature is raised. When a specific temperature T_c is reached such that

$$T_c - \Delta H_p/\Delta S_p \qquad (56)$$

ΔG_p changes from negative to positive, being 0 at T_c, so that the system is in equilibrium. Thus no polymerization can occur at temperatures higher than T_c, which is called a ceiling temperature (see POLYMERIZATION THERMODYNAMICS). The existence of such a temperature is a direct consequence of the fact that polymerization is an aggregation process.

Ceiling temperature phenomena may readily be visualized kinetically. It is necessary to take into account the depropagation reaction (eq. 57):

$$\dot{R}_{r+1} \xrightarrow{k_{dp}} \dot{R}_r + M \qquad (57)$$

The energy of activation of reaction 57 (E_{dp}) is generally much higher than that of propagation E_p, the difference being equal to the enthalpy change on polymerization (for long chains)

$$E_p - E_{dp} = \Delta H_p \qquad (58)$$

which is a relatively large quantity. Consequently, with increasing temperature k_{dp} increases rapidly relative to k_p, and although depropagation is normally negligible, it becomes significant at elevated temperatures.

Early experimental evidence pointed to the existence of a ceiling temperature when, during studies of the copolymerizations of low alkenes with sulfur dioxide, copolymerization only occurred below a fairly well-defined temperature characteristic of the particular olefin. Results were independent of the initiating system employed, indicating that the ceiling temperature phenomenon is a genuine characteristic of the system not caused by impurities.

With many monomers the equilibrium monomer concentrations at ambient temperatures are too small to measure directly since the ceiling temperatures are relatively high; they may be obtained by extrapolation. The ceiling temperature is a function of monomer concentration and is independent of mechanism. It is given by

$$T_c = \frac{\Delta H_p}{\Delta S_p^0 + R \ln [M]} \qquad (59)$$

Chain Transfer. Chain transfer is an atom abstraction process that may involve any species present in the polymeriza-

tion, including monomer and initiator. The transfer constant $C = k_f/k_p$, as defined, is a measure of the relative reactivities of the propagating radicals in transfer and in addition to the monomer. Transfer constants play an important part in discussions of the reactivities of radicals and monomers, and since polymer molar masses are dependent on the incidence of chain transfer, knowledge of the transfer activities of the components of a system is essential if polymers of specified mean size are to be prepared. Transfer constants cover an extremely wide range, from low values of a few units of 10^{-4} up to several hundreds or even thousands. Equation 11a is probably the most widely used relation in determining transfer constants.

Catalyzed Chain Transfer to Monomer. A report in 1981 on the catalyzed chain transfer to monomer in the free-radical polymerization of methyl methacrylate stimulated interest in this type of process. The remarkable catalytic activity of Co(II) hematoporphyrin IX tetramethyl ether (Co-Por) at concentrations in the range 10^{-4}–$10^{-3}M$ was demonstrated in the polymerization of MMA at 60°C initiated by azobisisobutyronitrile; it was found that the degree of polymerization (at high conversion) fell from 4,000 in the absence of Co-Por to approximately 8 when the cobalt catalyst was present.

The effect was shown to be genuinely catalytic; the concentration of Co-Por estimated spectrophotometrically did not change during reaction, and effectively all the material could be extracted unchanged at the end of the process. Co-Por is not an initiator and it was reported to have little influence on the rate of reaction. Since the only potential transfer agent present in sufficient concentration in these experiments was monomer, the results must be attributable to chain transfer to monomer catalyzed by Co-Por. The rate of polymerization was proportional to $[AIBN]^{1/2}$ throughout, indicating the absence of retardation, and the gel effect, normally so prominent in the polymerization of MMA at high conversion, was eliminated by the presence of Co-Por at a concentration 6.6×10^{-4}. The latter effect arises from the reduction in polymer molar mass.

Nmr studies of the polymers revealed that the transfer process is hydrogen atom transfer from propagating radical to monomer:

$$(60)$$

$$(R_1)$$
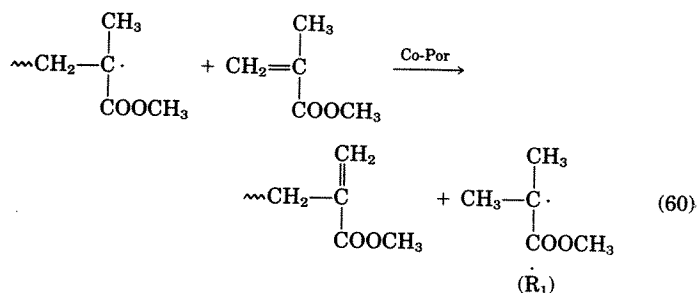
The transfer constant $C_{por} = 2.4 \times 10^3$ in the range 40–70°C. Reactions of this type have potential uses in synthesis, eg, macromer preparation.
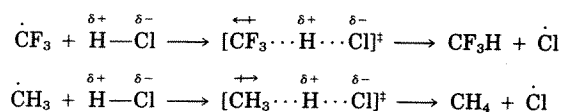
Reactivities of Radicals in Transfer Processes. Systematic consideration of atom abstraction reactions started with the formulation in 1938 of the Evans-Polanyi relation (eq. 61), which relates the activation energy E_A to the total enthalpy change ΔH^0. This relation is still the most general basis for discussion of transfer reactions.

$$E_A = \alpha \Delta H^0 + C \qquad (61)$$

It was derived from consideration of the potential energy curves of closely similar reactions; provided these curves do not change shape basically from one reaction to another, equation 61 follows from geometric arguments, α and C being constants. The parameter α is less than unity and should be larger for series of reactions with greater activation energies.

Relations of the Evans-Polanyi type are obscured if the potential energy curves for a series of reactions are dissimilar in shape. This may be brought about by (irregular) polarity changes from one reaction to another or by steric or electron delocalization changes.

Polar factors are important in transfer as in propagation processes. An example in small-radical chemistry, where the effect is well documented, is provided by hydrogen abstraction from methane and hydrogen chloride by methyl and trifluoromethyl radicals. The reactions are almost thermoneutral, and the activation energies are shown in Table 3. The low activation energies of the reactions with HCl are attributable to polar factors in the transition state:

$$\dot{C}F_3 + \overset{\delta+}{H}\!-\!\overset{\delta-}{Cl} \longrightarrow [CF_3\overset{\leftrightarrow}{\cdots}\overset{\delta+}{H}\cdots\overset{\delta-}{Cl}]^{\ddagger} \longrightarrow CF_3H + \dot{C}l$$

$$\dot{C}H_3 + \overset{\delta+}{H}\!-\!\overset{\delta-}{Cl} \longrightarrow [CH_3\overset{\leftrightarrow}{\cdots}\overset{\delta+}{H}\cdots\overset{\delta-}{Cl}]^{\ddagger} \longrightarrow CH_4 + \dot{C}l$$

Steric effects may be of three types: (1) steric hindrance, impeding the approach of the radical to the reaction site; (2) steric inhibition of resonance; and (3) steric compression. The latter seems to be of rather general importance; release of steric compression on radical formation accounts in part for the progressive decrease in C—H bond strength from primary to secondary and tertiary. The high transfer activities of carbon tetrabromide and mercaptans must be partly attributable to the relative weakness of the C—Br and S—H bonds undergoing scission in the compounds, but release of steric compressions in CBr_4 on radical formation is also likely to contribute. In the copolymerization of styrene and methyl methacrylate the penultimate unit effect in chain transfer with CBr_4 probably arises partly from steric compression in the transition state by close contacts of α-CH$_3$ and Br and partly from steric hindrance.

Electron delocalization in the addend or attacking radical influences the rate of transfer through its effects on bond dissociation energies. In the addend, delocalization reduces the strength of the bond being broken and so enhances transfer.

Chain transfer to halogen derivatives is frequently encountered in polymerizations. Halogen abstraction has been studied in connection with the radical chain addition of polyhalomethanes to olefins. Abstraction follows the order of strengths of the bonds being broken, except for hydrogen abstraction:

$$I > Br \sim H > Cl > F$$

Abstraction from halides by methyl radicals has been investigated. It appears that $\dot{C}H_3$ experiences a polar repulsion by the filled orbitals of the halogen atom. Since this would not arise between $\dot{C}H_3$ and H—R, the rate of abstraction of hydrogen is greater than expected on the basis of bond dissociation energy alone. Other results with $\dot{C}F_3$ are also consistent with this view.

Quantum mechanical studies of hydrogen abstraction from alkenes have been published.

Empirical Relations for Radical and Monomer Reactivities. Empirical schemes have existed for many years; they do not have a firm theoretical basis, but they have proved of value, both in making predictions and in summarizing data.

The Q-e Scheme. The alternating tendency in radical copolymerization, first demonstrated by Mayo and Walling, is most easily accounted for in terms of differing electrical polarities. Alfrey and Price embodied this idea into the *Q-e* scheme, which was developed to allow semiquantitative prediction of reactivity ratios.

Three aspects of the *Q-e* scheme have attracted criticism: first, the assumption of equal charges for radical and monomer; secondly, the assumption of permanent charge, present in the ground-state reactants, rather than transition state polarity; and thirdly, the observed (effective) independence of the dielectric constant of the medium shown by reactivity ratios. Although these criticisms are mainly valid, they do not reduce the practical value of the *Q-e* scheme or alter the fact that it is in harmony with much experimental data.

Patterns of Free-radical Activity. The "Patterns" scheme was devised as a semiempirical approach in which arbitrary features were reduced to a minimum. As in the *Q-e* treatment, the reaction rate was considered to be determined by the general reactivities of the radical and the substrate together with the appropriate polarities, but both types of property were so defined as to make independent experimental measurements possible. The considerations in "Patterns" apply equally well to propagation and transfer reactions.

Other Models and Treatments. Several models for the theoretical treatment of reactivity ratios have been proposed, including the electronegativity model, the charge-transfer model, and a model based on a modified Hammett equation.

Bimolecular Termination. Polymer radicals, like small radicals in the gas or liquid phases, may interact by combination and/or disproportionation. The two processes give rise to unusual groups in the polymer chains—a head-to-head sequence statistically in the middle of the chain or a terminal double bond and a saturated end group, for combination or disproportionation respectively. Such groups influence the properties of the polymers, sometimes to an unduly large extent. Unsaturated end groups in poly(methyl methacrylate) are preferred sites for the initiation of thermal degradation; they may also participate in polymerization and so influence the molar weight

Table 3. Hydrogen Abstraction Reactions

Reaction	Activation energy, kJ/mol[a]
$CH_4 + \dot{C}H_3 \longrightarrow \dot{C}H_3 + CH_4$	58.6
$CH_4 + \dot{C}F_3 \longrightarrow \dot{C}H_3 + CF_3H$	46.9
$HCl + \dot{C}H_3 \longrightarrow \dot{C}l + CH_4$	10.5
$HCl + \dot{C}F_3 \longrightarrow \dot{C}l + CF_3H$	20.9

[a] To convert kJ/mol to kcal/mol, divide by 4.184.

distribution and contribute to branching and gelation. Head-to-head sequences can also lead to thermal instability by virtue of the steric compression they introduce. Further, the molar mass distribution of the polymer is determined by the mode of termination, in the absence of predominating transfer.

The nature of the termination reaction is therefore not merely a matter of academic interest but, like initiation, has numerous practical implications.

Determination of the Disproportionation:Combination Ratio. A number of techniques for measuring $x = k_{td}/(k_{tc} + k_{td})$ are available, but there is a disappointing lack of firm information for many monomers. Techniques include calculation from DP, measurement of $\bar{P}_w/\bar{P}_n$, the kinetic method, coupling experiments, grafting tests, gelation experiments, and model experiments with small radicals.

Diffusion Control in Bimolecular Termination. It is generally agreed that termination reactions of small radicals in solution are diffusion-controlled.

Diffusion control occurs when the rate of an inherently fast process is limited by the rate of approach of the reacting entities to the proximity required for reaction.

Bimolecular termination reactions between macromolecular radicals may be visualized as follows. First, two macromolecules must come into contact by translational diffusion; secondly, the reactive ends of the chains must diffuse sufficiently closely and in a suitable configuration to allow reaction, which is stage three. If chemical reaction is slow compared to either diffusion process, it is rate-controlling, but if the chemical reaction is relatively fast, the rate of the overall process becomes diffusion-controlled by either of the diffusion steps mentioned. Several lines of experimental evidence point to segmental diffusion as the critical step.

Theoretical calculations have given complicated results, but suggest that the termination coefficient is inversely proportional to solvent viscosity (as found experimentally) and is influenced by the molar masses of the polymer radicals, decreasing somewhat as the latter increase. It is also affected by excluded volume, chain flexibility, monomer size, and the thermodynamic quality of the solvent.

Theoretically derived equations are too complex to use in kinetic schemes. An empirical relation which has received considerable attention is the geometric mean expression

$$k_t \propto (rs)^{-b}$$

where r,s are the sizes of the reacting radicals and b is a small positive quantity of the order 0.1.

Polymerization at High Conversion

Optimization of a commercial process that necessitates achievement of high conversions requires a model that enables the course of reaction to be calculated over the whole range of conversion. The model should contain the minimum number of adjustable parameters, be independent of type and concentrations of initiator, and allow calculation as functions of time of molecular weight distributions as well as conversions.

Development of a suitable model evidently involves estimation of termination coefficients at high polymer concentrations, but account must also be taken of diffusion control of the propagation reaction which sets in at very high viscosities. When polymerization at a temperature below the glass transition temperature of the polymer is taken to high conversion, a stage is reached at which the reaction mixture assumes glassy

conditions, with residual monomer acting as plasticizer. The propagation rate then becomes diffusion-controlled and may fall to near-zero values, so that polymerization virtually ceases, even though the conversion is less than 100%. This phenomenon is the glass effect; it must not be confused with dead-end polymerization arising from initiator depletion, discussed earlier.

Rather than attempt a mechanistic model, necessarily very complex, it may be more realistic to adopt a semiempirical approach. The "free-volume" treatment assumes that control by translational diffusion occurs when the diffusion coefficient of a polymer radical D_P becomes less than or equal to a critical value D_{Pcr}. After the start of this diffusion control, k_t is assumed proportional to the diffusion coefficient

$$k_t = k_1 D_P \qquad (D_P < D_{Pcr}) \qquad (62)$$

k_1 being a constant. D_P is related to the free-volume fraction V_F by the equation

$$D_P = \frac{\varphi_0 \delta^2}{k_2 M} \exp\left(-A/V_F\right) \qquad (63)$$

where M is the (homogeneous) polymer molar mass; φ_0 and δ the jump frequency and distance respectively; k_2 and A constants. The free volume is a function *inter alia* of the volume fraction of polymer, and so decreases during polymerization in a manner which may be represented by the relation:

$$V_F = \{0.025 + \alpha_P(T - T_{gP})\} \frac{V_P}{V_T}$$

$$+ \{0.025 + \alpha_M(T - T_{gM})\} \frac{V_M}{V_T}$$

$$+ \{0.025 + \alpha_S(T - T_{gS})\} \frac{V_S}{V_T} \qquad (64)$$

in which V, T_g, and α represent volume, glass-transition temperature, and coefficient of thermal expansion respectively; and the subscripts P, M, S denote polymer, monomer, and solvent respectively. V_T is the total volume. The best correlation with experimental data is achieved when M in equation 63 is replaced by the square root of the cumulative weight-average molar mass $\bar{\bar{M}}_w$; hence

$$k_t = k_1 \left(\frac{\varphi_0 \delta^2}{k_2 \bar{\bar{M}}_w^{1/2}}\right) \exp\left(-A/V_F\right) \qquad (65)$$

in the absence of chain entanglements. When chain entanglements occur, probably soon after k_t becomes controlled by translational diffusion, then the relation

$$k_t = \bar{k}_1 \left(\frac{\varphi_0 \delta^2}{\bar{k}_2 \bar{\bar{M}}_w^{1.75}}\right) \exp\left(-A/V_F\right) \qquad (66)$$

in which $\bar{k}_1$ and $\bar{k}_2$ are constants is used. If it is assumed that termination becomes translation-diffusion-controlled before occurrence of entanglements, then at the onset of the gel effect

$$\bar{\bar{M}}_w^m \exp\left(A/V_F\right) = \frac{k_1 \varphi_0 \delta^2}{k_{t0} k_2} = K_3 \qquad (67)$$

K_3 being a (temperature-dependent) constant and k_{t0} the value of k_t not influenced by entanglements. According to equation

65, $m = 0.5$, but in equation 67 this quantity is kept as an adjustable model parameter. The cumulative molecular weight and free volume at this critical point are designated $\overline{M}_{wcr1}$ and V_{Fcr1} respectively; these quantities satisfy equation 67. For each weight-average molecular weight, at constant temperature there is one and only one conversion satisfying equation 67. As the polymerization proceeds, from equations 66 and 67

$$\frac{k_t}{k_{t0}} = \left(\frac{\overline{M}_{wcr1}}{\overline{M}_w}\right)^n \exp\left[-A\left(\frac{1}{V_F} - \frac{1}{V_{Fcr1}}\right)\right] \quad (68)$$

in which $n = 1.75$ according to equation 66 but is retained as a model parameter.

An expression analogous to equation 68 may be written for the propagation coefficient, when this becomes diffusion-controlled, with the aid of the expression for the diffusion coefficient D_M of a small molecule in a polymer solution (φ_2, δ_2 being jump frequency and distance, respectively, and B a constant):

$$D_M = \left(\frac{\varphi_2 \delta_2^2}{6}\right) \exp\left(-\frac{B}{V_F}\right) \quad (69)$$

If V_{Fcr2} is the critical volume corresponding to the conversion at which diffusion control sets in,

$$k_p = k_{p0} \exp\left[-B\left(\frac{1}{V_F} - \frac{1}{V_{Fcr2}}\right)\right] \quad (70)$$

k_{p0} being the propagation coefficient at low conversions.

Insertion of k_t and k_p given by equations 68 and 70 into the classical rate expression gives for the rate of reaction

$$\frac{dx}{dt} = \left(\frac{k_{p0}^2}{k_{t0}}\right)^{1/2} \left(\frac{\overline{M}_w}{\overline{M}_{wcr1}}\right)^{n/2} \exp\left[-B\left(\frac{1}{V_F} - \frac{1}{V_{Fcr2}}\right)\right]$$

$$\times \exp\left[\frac{A}{2}\left(\frac{1}{V_F} - \frac{1}{V_{Fcr1}}\right)\right] \left[\frac{fk_d[I]_0}{1 - \epsilon x}\right]^{1/2} (1 - x)\exp\left(-\frac{k_d t}{2}\right) \quad (71)$$

In this equation x is the fractional conversion and ϵ is the volume contraction factor ($= (d_p - d_M)/d_p$, the ds being densities).

Since k_t is a function not only of conversion and temperature but also of molecular weight, the latter must be estimated. Instantaneous values of $\overline{M}_w$ are calculated in the conventional manner and the required cumulative values obtained from the relation

$$\overline{M}_w = \frac{1}{x} \int_0^x \overline{M}_w dx \quad (72)$$

Conversion is calculated as a function of time by simultaneous solution of equations 71 and 72 with the aid of an iterative procedure.

The model has been tested for a variety of polymerizations taken to high conversion, including those of methyl methacrylate and styrene and has given good agreement with experimental data obtained in bulk and solution polymerization over wide ranges of temperature and initiator and solvent concentrations.

Heterogeneous Radical (Precipitation) Polymerization

Radical Occlusion and Living Macroradicals. The discussions on the termination reaction and on polymerizations carried to

high conversions have illustrated the importance of physical conditions on the course of polymerization. Heterogeneous radical polymerizations supply further illustrations, sometimes of an extreme kind. Heterogeneous polymerizations may be defined as those polymerizations in which propagating radicals pass from one phase to another. Often heterogeneity results from the separation of solid polymer from monomer initially present in bulk or in solution or in the gas phase.

Heterogeneous polymerizations as a class show characteristic types of behavior, among which are autoacceleration with time, from the onset of heterogeneity to appreciable degrees of conversion; initiator exponents exceeding 0.5 (the classical value); and unexpectedly large photochemical aftereffects ΔM_{aft}, which increase with the duration of irradiation. These features are not due to the initial presence of impurities but are associated with polymer separation during reaction.

The notion of radical occlusion arose from consideration of the behavior of acrylonitrile on polymerization. Radicals are trapped in the polymer during photopolymerization at 25°C; the concentrations of such radicals have been determined by "titration" with DPPH and by esr observations. The active polymer is indefinitely stable in contact with monomer at 25°C, but rapidly becomes deactivated by contact with air or oxygen. Clearly, at 25°C the radicals are protected from contact with monomer by the surrounding polymer chains, the system showing glass effect behavior. At 60°C the polymer swells sufficiently to admit monomer and allow reaction (the so-called "fast reaction"). At the end of the fast reaction at 60°C, no radicals survive. The active polymer is to be regarded as a living radical polymer.

Occlusion and Polymerization Kinetics. The "occlusion" picture of heterogeneous polymerization was built up from consideration of phenomena of the kind described. It is based on the idea that many (or all) polymer radicals precipitate during growth; in the nonsolvent environment, the precipitated chains tend to be tightly coiled and since the radical end has a high probability of being occluded ("shut up") within the coil, it will be shielded from attack and so appear unreactive.

The mean degree of occlusion influences the kinetic coefficients k_p and k_t and is thus responsible for the characteristic kinetic features discussed. The incidence of occlusion is also evident in the effects of low concentrations of swelling agents on the rate of polymerization of acrylonitrile at 25°C and the unusual dependence on temperature of the molecular weight of polyacrylonitrile prepared at constant initiator concentration.

The influence of occlusion on the overall kinetics of polymerization is easy to appreciate in a qualitative fashion. As polymerization proceeds, the number of polymer particles present and their average size increase. Both factors increase the mean degree of occlusion; hence the effective k_t diminishes and the rate of polymerization increases.

Block Copolymers from Macroradicals. Living polyacrylonitrile and polyacrylamide have been prepared and the macroradicals used to initiate block polymerization. Methyl methacrylate and methyl acrylate were more active in these reactions than vinyl acetate, vinylidene chloride, or styrene.

Molar Mass Distributions

As has been discussed, stationary conditions in a free-radical polymerization are normally established in a short time after the start of reaction. Subsequently, in the stationary phase of the reaction, the molar masses of the polymeric products change

only slowly, corresponding to the consumption of the reactants. If the concentrations change only slightly or are maintained constant, the molar masses remain effectively constant and the number-average degrees of polymerization $\bar{P}_n$ are given by equation 11. This is the origin of the familiar comment that high polymers are formed (almost) instantaneously in radical polymerizations, but in living ionic systems or condensation polymerizations, the molar masses increase throughout the course of the reaction.

Polymerization is governed by statistical laws, and since a growing radical is confronted by several possibilities, the radicals present and also the dead polymer formed have sizes distributed over a range extending from a single unit upwards. (Note the difference from living systems, in which, ideally, propagation is the only reaction possible.) When all concentrations are effectively constant or maintained constant, the distribution (at low conversion) is given by

$$P_r = \frac{\Delta M}{k_p M}(1 - \xi)\xi^r \left\{ k_{fM}M + k_{fS}S + k_{t_d}\left(\frac{\phi}{k_t}\right)^{1/2} \right.$$
$$\left. + \frac{k_{t_c}}{2}\left(\frac{\phi}{k_t}\right)^{1/2}(r - 1)\frac{1 - \xi}{\xi}\right\} \qquad (73)$$

where M is the concentration of monomer polymerized and P_r is the concentration of polymer molecules of size r formed. ξ is the probability of propagation:

$$\xi = k_p M/\{(k_p M + k_{fM}M + k_{fS}S + (Jk_r)^{1/2}\} \qquad (74)$$

For termination by disproportionation, with or without transfer, the number and weight averages are given by

$$\frac{\bar{r}}{(\text{disp,trans})} = \frac{1}{1 - \xi}$$
$$\frac{\bar{r}_w}{(\text{disp,trans})} = \frac{1 + \xi}{1 - \xi} \sim \frac{2}{1 - \xi} \text{ for long chains} \qquad (75)$$

while for termination by exclusive combination without transfer

$$\frac{\bar{r}}{(\text{comb})} = \frac{2}{1 - \xi}$$
$$\frac{\bar{r}_w}{(\text{comb})} = \frac{2 + \xi}{\xi(1 - \xi)} \sim \frac{3}{1 - \xi} \text{ for long chains} \qquad (76)$$

In a homogeneous polymer of degree of polymerization r, $\bar{r} = \bar{r}_w = r$; for heterogeneous polymers the magnitude of $\bar{r}_w/\bar{r}$ is often taken as a measure of heterogeneity, or breadth of the distribution. For disproportionation (transfer) and combination polymers of the ratios $\bar{r}_w/\bar{r}$ are respectively 2 and 1.5 (from eqs. 75, 76), so that on this criterion the latter has a narrower distribution.

Determination of Absolute Rate Coefficients

The most direct method is measurement of the propagating radical concentration, from which the absolute propagation coefficient may be evaluated by use of equation 10a if the rate of polymerization is known. Although this possibility has been recognized for many years, the low radical concentrations involved ($\sim 10^{-7}$ molar) have delayed its application; however,

sufficiently sensitive techniques for observing esr spectra have been developed.

The second type of method is based on kinetics. Inspection of the equations for stationary state condition shows that all the quantities that may be readily determined—the rate of polymerization, kinetic chain length, and polymer molar mass—involve the propagation and and termination coefficients as $k_p/k_t^{1/2}$, so that the two quantities cannot be separated on the basis of these observations. Measurements of transfer coefficients provide ratios (k_p/k_{fM}, k_p/k_{fS}) and not absolute values. On the other hand, properties measured under nonstationary conditions are expressible in terms of k_p/k_t, eg, the pre- and aftereffects, so that combination of stationary and nonstationary data allows separate evaluations of the rate coefficients. A number of procedures for making the nonstationary observations have been devised, including direct measurement of radical concentrations, and kinetic methods (eg, measuring, pre- and aftereffects, the viscosity method), and the rotating sector technique. Note that the kinetic problem of separating the rate coefficients is encountered in radical chain reactions in general.

BIBLIOGRAPHY

P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., 1953.

C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, *The Kinetics of Vinyl Polymerization by Radical Mechanisms*, Butterworths, London, 1958.

C. H. Bamford and C. F. H. Tipper, eds., *Comprehensive Chemical Kinetics*, Vol. 14A, Elsevier, Amsterdam, 1976.

G. Odian, *Principles of Polymerization*, 2nd ed., John Wiley & Sons, Inc., New York, 1981.

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RADIOPAQUE POLYMERS

The search for a nondestructive method of polymer evaluation has led to a new area of research, that of radiopaque polymers. Based on casting shadows, radiographic imaging techniques incorporate the principle of radiopacity, which is the physical property of absorbing x rays or reflecting ultrasound waves. Both of these techniques depend on variations in densities between a specimen and its surroundings. Sharp x-ray imaging is obtained from materials of high electron density; effective ultrasound is observed only when significant variations in specific gravity exist between an object and its surroundings.

Conventional polymers cannot be detected by imaging techniques because they mainly contain the elements carbon, hydrogen, oxygen, and nitrogen, which exhibit both low electron density and low specific gravity. The recent research into radiopaque polymers explores methods of increasing the average electron density and the specific gravity of polymers by incorporating heavy elements into these systems.

Physical Principles of X-ray and Ultrasound Imaging

X-ray Imaging. Examination of structures by casting shadows was the underlying principle of all x-ray imaging for approximately 80 years, until in the mid-1970s a new imaging